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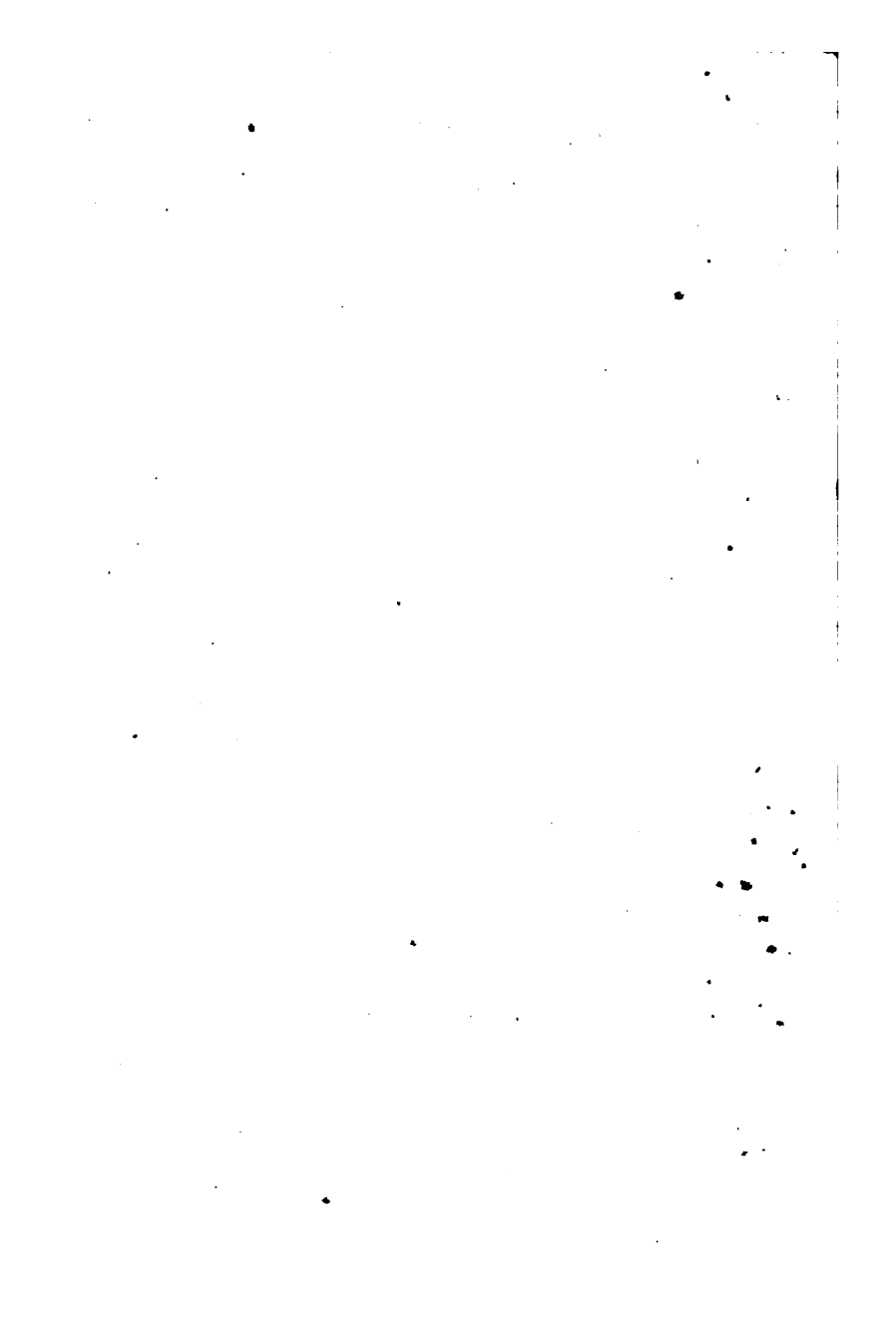
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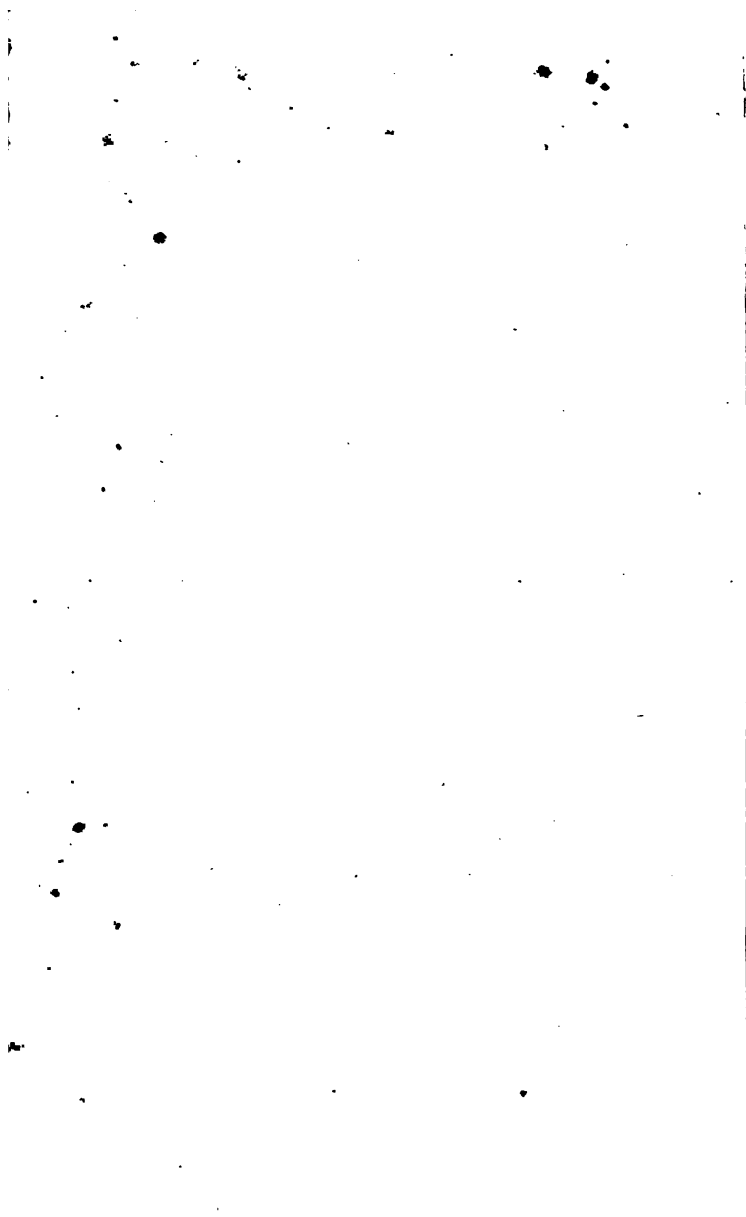
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ELEMENTARY  
INORGANIC CHEMISTRY:  
THE NON-METALLIC ELEMENTS.

BY

RAPHAEL MELDOLA, F.C.S.,

*Royal College of Chemistry and Science Training Schools, South Kensington.*



London:

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## PREFACE.

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THIS book makes no pretence to teach practical Chemistry, but is intended rather as a companion to the student when attending the course of demonstrations prescribed by Dr. Frankland for the science classes undergoing preparation for the May examinations of the Science and Art Department (Directory, p. 107). It is for this reason that the description of practical details (which can be acquired by experience much more readily than from books) has been reduced to a minimum. The contents of this book will, it is hoped, suffice to carry the student through the elementary stage, and, with a little amplification on the part of the teacher, also through the advanced stage of the May examination in Inorganic Chemistry. For the honours examination larger manuals must be consulted; and to these it is hoped the present volume may be found a useful introduction.

I have intentionally departed from the order of subjects as given in the Directory, being of opinion that the compilation of a book supplying only that amount of knowledge required by the Department in the precise Directory order, tends rather to encourage a "getting-up" of just those subjects required than to a conscientious study of the science. To offer a check to this system of acquiring knowledge under high-pressure—now unfortunately too common—I have endeavoured to make of this little work as connected a whole as possible, and in so doing I venture to hope that it will be found of service to a wider class of students than that for which it was more particularly written.

The close relationship between the sciences of Chemistry and Physics has convinced me that some preliminary knowledge of this latter science is of immense service—nay, is almost indispensable to the would-be student of Chemistry. Many of the most powerful arguments in favour of the theory of the existence of molecules rest upon physical grounds. The force of *heat*, the most powerful agent in the production of chemical change, is essentially a physical force: so also is *electricity*, now yielding such interesting results as a synthetical agent in the hands of Sir Benjamin Brodie; and so also is *light*. Should not then the student of Chemistry, who is daily made to witness the chemical changes wrought by these physical forces, possess some knowledge of the laws by which they are governed?

Students presenting themselves for examination in Zoology are expected by the Department to have received instruction in Animal Physiology (Directory, p. 184). I venture to think that an elementary knowledge of Physics would be of almost equal service to the chemical candidate.



The difference of opinion among modern chemists as to the truth of the atomic theory leads me to say a word or two on this important subject here. For having adopted this theory in the present manual hardly any excuse can be considered necessary, since, although its *truth* may be disputed, its *utility* cannot be the subject of a doubt. The truth of a theory is one thing, its service to science is another. Till very recently electricians made use of the "fluid" theory, although they knew that in all probability this theory was untrue; yet it was useful as serving to explain the large body of facts belonging to electrical science. How much more, then, is Chemistry in need of some theory to cement together in the mind its vast and ever-increasing body of facts!

From this standpoint of utility alone are we justified in retaining the theory; indeed, were it proved to be untrue to-morrow, we should still be justified in using it until some equally satisfactory explanation of chemical phenomena was forthcoming. When, however, we reflect upon the large number of distinct classes of facts capable of being explained by the atomic theory; when we consider the power of prediction that it gives us in the case of isomeric bodies, we cannot but admit that if not literally true, this theory is probably symbolic of, or runs parallel with, the cause or causes of chemical phenomena. In a lecture "On Some Points of the Theoretic Teaching of Chemistry," Professor Cannizzaro, of Palermo, states, "I do not hesitate to assert that the theory of atoms and molecules ought to play in the teaching of chemistry a part analogous to that of the theory of vibrations in the teaching of optics." And again:—"After many trials in the course of my teaching, I have come to the conclusion, that not only is it impossible to eliminate the atomic theory altogether, but, moreover, that in order to arrive at this theory, it is not desirable to follow the long and fatiguing road of induction. On the contrary, it is better to get to it as quickly as possible, by one of those short cuts which the human mind often takes in order to raise itself quickly to a height from which the relations between phenomena can be discerned at a glance."

Dr. Frankland has been so kind as to look through the proof sheets of Appendix III., and the calculations in Chapter IV. have been verified by my friend Mr. Thomas Bolas, F.C.S., to whom my thanks are due.

LONDON, Nov., 1873.

R. M.

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<sup>1</sup> The Faraday lecture, delivered before the Chemical Society, May 30th, 1873.

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# INORGANIC CHEMISTRY.

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## INTRODUCTION.

**Definition and Scope of the Science.**—The objects which surround us on all sides, and which we can see, handle, or weigh, constitute what is termed *matter*; and *Chemistry is the science which treats of the nature and properties of matter under its various forms and combinations*. If we apply heat to a piece of ice, we convert it into liquid *water*; and if this liquid be still further heated, we convert it into a vapour called *steam*. Now, it is easily demonstrable that ice and steam are but different forms of the same substance—water; for by cooling the steam we convert it again into water, and the water thus obtained can, by further cooling, be solidified into ice. The changes here described are *physical*<sup>1</sup> changes, and belong to the science of *Physics*, which treats of the temporary changes produced by the action of force upon matter. If, however, we apply a degree of heat far greater than is necessary to cause water to boil—say a heat of an intense whiteness—to the water vapour, we shall find that it undergoes a remarkable and permanent change in its properties. It now no longer yields water on cooling, but remains a permanent gas; and the application of a lighted taper will convince us that this gas possesses explosive properties not possessed by the original steam. The steam is, in this instance, said to have undergone a *chemical* change, and we thus learn that chemical action is quite different

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<sup>1</sup> G. *physis*, nature.

from physical action, inasmuch as the changes wrought by it in matter are of a *permanent* instead of a *temporary* nature, and that while *Physics* treats of the temporary changes produced in matter by the action of forces, *Chemistry* includes all cases in which permanent change is produced in matter, either by the action of physical forces, or by the action of the various forms of matter upon each other.

**Division of the Subject.**—The science of Chemistry is usually divided into two branches—the study of the materials composing *dead* matter, and the study of the materials composing *living* matter. The former treats of the forms of matter composing the solid crust of the earth, its rocks and minerals, its atmosphere and its waters; the latter treats of the materials entering into the composition of animals and plants, together with other compounds that are obtainable from these by artificial means. The former division is termed *inorganic*, or *mineral* chemistry, and the latter is known as *organic*<sup>1</sup> chemistry. We shall treat of inorganic chemistry only in the present volume.

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<sup>1</sup> G. *organon*, an instrument; applied to living things because they are in general possessed of certain structures, or organs, suitable for the discharging of certain functions.

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## CHAPTER I.

### ON MATTER AND ITS COMBINING LAWS.

---

#### A.—CONSTITUTION OF MATTER.

**Simple and Compound Matter.**—It is found by chemists that while some of the bodies they examine are capable of being separated into two or more substances, others resist all attempts at separation. The latter are termed *elements*, or “simple bodies;” the former, “compound bodies.” The substances at present regarded as elementary are sixty-three in number, and all the matter in the globe, whether organic or inorganic, consists of these elements, either in the free state or in combinations of two, three, four, &c. In other words, matter presents itself as either *simple* or *compound*.

The elements present, among themselves, a great variety of characters. At ordinary temperatures some are solid, others liquid, and others gaseous. Some of the elements, ordinarily gases, can be reduced to the liquid state by great cold and pressure, while others have withstood all attempts at liquefaction. Some elementary bodies are good conductors of heat and electricity; others are bad conductors of these forces: some allow light to pass through them, or are transparent; others obstruct its passage, or are opaque: some elements are attracted by the magnet, while others are repelled by it.<sup>1</sup> With regard to their occurrence in nature, the elementary bodies are in some cases universally distributed and very abundant, while in other cases they are widely distributed, and yet

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<sup>1</sup> For further particulars on these subjects see the volumes on Natural Philosophy in this series.

occur in extremely small quantities; while again, in other cases, they are both limited in distribution and occur in minute traces.

**Chemical Affinity.**—The power or force which holds together the elements of a compound, or which resists their separation when once combined, is termed *chemical affinity*,<sup>1</sup> or chemical attraction. Such forces as gravitation, heat, light, electricity, and magnetism, act through distances more or less great; the force of chemical affinity, on the other hand, acts only through portions of space inappreciable by us. Thus, while a hot iron causes the quicksilver to rise in a thermometer several inches distant from it, copper filings and sulphur,<sup>2</sup> which possess a great affinity for each other, may be mixed together without combination taking place, simply because the mechanical action to which they are submitted does not bring these substances within the sphere of each other's attraction. Owing to this fact that chemical affinity acts only at insensible distances, substances that we wish to act upon one another chemically are brought together, where possible, either in the state of a liquid or of a gas, as their particles have then greater freedom of motion.

*The compound produced when chemical union takes place exhibits properties entirely different from those of either of its constituents.* This is the chief characteristic of chemical action. If, for instance, the copper filings and sulphur above alluded to be heated together, they combine chemically, and a black powder, having neither the properties of copper nor of sulphur, is produced. Thus, by chemical action, the most wonderful transformations are effected. Bodies having no odour combine and produce a compound whose odour is unbearable. Two tasteless substances produce a body of an

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<sup>1</sup> L. *affinitas*, relationship.

<sup>2</sup> This is another name for the familiar substance, *brimstone*.

intense taste: two liquids may produce a solid, and *vice versa*:<sup>1</sup> two invisible gases may produce a gas having a deep colour: the same elements which compose sugar, starch, and gum, when united in different proportions, form the poisonous oxalic acid and the intoxicating alcohol. These, and the numerous examples which we shall meet with in studying the elements and their compounds in greater detail in future chapters, will serve to impress the student with the extent of the changes brought about by chemical combination.

The force with which the various elements unite with one another is of varying degrees of intensity, and formerly chemical works contained tables supposed to display the *affinities* of the elements. It has been shown by modern chemists, however, that such tables of affinities cannot obtain, since the attraction of one element for another depends to a very great extent upon the *physical conditions* under which the elements are made to act upon one another. Of this fact we shall meet with numerous illustrations hereafter.

The forces of *heat* and *light* in some instances decompose<sup>2</sup> compounds into their constituent elements: in other cases these forces cause the elementary bodies to combine. *Electricity* usually exerts a decomposing influence on chemical compounds when these are submitted to its action in a proper condition.

**Chemical Elements.**—It will be now necessary for the student to familiarise himself with the names of some of the more important elements, and for this purpose we give an alphabetically-arranged table containing a list of all the known elements. It is customary to divide the elementary bodies into *metals* and *non-metals*, or *metalloids*, but this division must be looked upon as entirely artificial, and as having been made more for convenience of description than for expressing

<sup>1</sup> L. the other way about.

<sup>2</sup> L. *de*, from, and *compono*, to place together.



any natural distinction existing between these two classes of bodies. In the subjoined table the non-metals are printed in capitals, the commoner metals in small letters, and the rare metals in italics:—

TABLE OF THE CHEMICAL ELEMENTS.

Name of Element.	Symbol.	Combining weight.
Aluminium ..	Al ..	27.4
Antimony ..	Sb <sup>1</sup> ..	122
ARSENIC ..	As ..	75
Barium ..	Ba ..	137
Bismuth ..	Bi ..	210
BORON ..	B ..	11
BROMINE ..	Br ..	80
<i>Cadmium</i> ..	Cd ..	112
<i>Cæsium</i> ..	Cs ..	133
Calcium ..	Ca ..	40
CARBON ..	C ..	12
<i>Cerium</i> ..	Ce ..	92
CHLORINE ..	Cl ..	35.5
Chromium ..	Cr ..	52.2
Cobalt ..	Co ..	58.8
Copper ..	Cu <sup>2</sup> ..	63.5
<i>Didymium</i> ..	D ..	95
<i>Erbium</i> ..	E ..	112.6
FLUORINE ..	F ..	19
Glucinum ..	Gl ..	9.4
Gold ..	Au <sup>3</sup> ..	197
HYDROGEN ..	H ..	1
<i>Indium</i> ..	In ..	198
IODINE ..	I ..	127
<i>Iridium</i> ..	Ir ..	198
Iron ..	Fe <sup>4</sup> ..	56
<i>Lanthanum</i> ..	La ..	90.2

<sup>1</sup> L. stibium.    <sup>2</sup> L. cuprum.    <sup>3</sup> L. aurum.    <sup>4</sup> L. ferrum.

TABLE OF THE CHEMICAL ELEMENTS (*continued*).

Name of Element.	Symbol.	#	Combining weight.
Lead .. ..	Pb <sup>1</sup> ...	..	207
<i>Lithium</i> .. ..	Li .. ..	..	7
Magnesium .. ..	Mg .. ..	..	24
Manganese .. ..	Mn .. ..	..	55
Mercury .. ..	Hg <sup>2</sup> .. ..	..	200
<i>Molybdenum</i> .. ..	Mo .. ..	..	96
Nickel .. ..	Ni .. ..	..	58.8
<i>Niobium</i> <sup>3</sup> .. ..	Nb .. ..	..	94
NITROGEN .. ..	N .. ..	..	14
<i>Osmium</i> .. ..	Os .. ..	..	199.2
OXYGEN .. ..	O .. ..	..	16
<i>Palladium</i> .. ..	Pd .. ..	..	106.6
PHOSPHORUS .. ..	P .. ..	..	31
Platinum .. ..	Pt .. ..	..	197.4
Potassium .. ..	K <sup>4</sup> .. ..	..	39.1
<i>Rhodium</i> .. ..	Rh .. ..	..	104.4
<i>Rubidium</i> .. ..	Rb .. ..	..	85.4
<i>Ruthenium</i> .. ..	Ru .. ..	..	104.4
SELENIUM .. ..	Se .. ..	..	79.4
SILICON .. ..	Si .. ..	..	28
Silver .. ..	Ag <sup>5</sup> .. ..	..	108
Sodium .. ..	Na <sup>6</sup> .. ..	..	23
Strontium ... ..	Sr .. ..	..	87.6
SULPHUR .. ..	S .. ..	..	32
<i>Tantalum</i> .. ..	Ta .. ..	..	182
TELLURIUM .. ..	Te .. ..	..	129
<i>Thallium</i> .. ..	Tl .. ..	..	203.6
<i>Thorium</i> .. ..	Th .. ..	..	231.5
Tin .. ..	Sn <sup>7</sup> .. ..	..	118
<i>Titanium</i> .. ..	Ti .. ..	..	50

<sup>1</sup> L. *plumbum*.<sup>5</sup> L. *argentum*.<sup>2</sup> L. *hydrargyrum*.<sup>6</sup> *Natrium*, from an Arabic word.<sup>3</sup> Called also Columbium.<sup>7</sup> L. *stannum*.<sup>4</sup> *Kalium*, from an Arabic word.

TABLE OF THE CHEMICAL ELEMENTS (*continued*).

Name of Element.	Symbol.	Combining weight.
<i>Tungsten</i> .. ..	W <sup>1</sup> .. ..	184
<i>Uranium</i> .. ..	U .. ..	120
<i>Vanadium</i> .. ..	V .. ..	51.3
<i>Yttrium</i> .. ..	Y .. ..	61.6
<i>Zinc</i> .. ..	Zn .. ..	65.2
<i>Zirconium</i> .. ..	Zr .. ..	89.6

B.—LAWS OF PONDERAL<sup>2</sup> COMBINATION.

(1) **Combining Weights.**—In the third column of the above table we have assigned to each element a certain number, called its *combining weight*: we have now to explain the meaning of this term.

It is found that when chemical union takes place, the elements concerned do not combine in indefinite quantities as in ordinary mixtures, but that combination always takes place in the ratio<sup>3</sup> of the numbers we have assigned or in some simple multiple of these quantities, which are hence called *combining weights*. Thus, from whatever source we obtain a chemical compound, it will be found that the same compound invariably contains the same elements united in the same proportion by weight; and this law of *constancy of composition* is one of the fundamental laws of chemical science.

(2) **Law of Multiple Proportions.**—It has just been stated that when the elementary bodies unite with each other, it is either in the proportion of their combining

<sup>1</sup> Called also Wolfram.

<sup>2</sup> *L. pondus*, weight; meaning, combination by weight.

<sup>3</sup> *L. ratio*, the relationship which one expression bears to another with regard to quantity.

weights or in some simple multiple of these numbers : it will now be necessary to study this law of combination in multiples of the combining weights in somewhat greater detail.

The element sulphur, whose combining weight is 32, forms no less than eight compounds with the elements hydrogen and oxygen, whose combining weights, as will be seen on referring to the Table of Elements, are respectively 1 and 16. Without, at this stage, burdening the mind of the student with the names of these compounds, the following table will serve to exhibit this increment of the sulphur and oxygen in multiples of their combining weights.

TABLE SHOWING COMPOUNDS OF SULPHUR WITH OXYGEN AND HYDROGEN.

Hydrogen.		Sulphur.		Oxygen.
I.— $1 \times 2 = 2$	..	$32 \times 1 = 32$	..	$16 \times 2 = 32$
II.— $1 \times 2 = 2$	..	$32 \times 1 = 32$	..	$16 \times 3 = 48$
III.— $1 \times 2 = 2$	..	$32 \times 1 = 32$	..	$16 \times 4 = 64$
IV.— $1 \times 2 = 2$	..	$32 \times 2 = 64$	..	$16 \times 3 = 48$
V.— $1 \times 2 = 2$	..	$32 \times 2 = 64$	..	$16 \times 6 = 96$
VI.— $1 \times 2 = 2$	..	$32 \times 3 = 96$	..	$16 \times 6 = 96$
VII.— $1 \times 2 = 2$	..	$32 \times 4 = 128$	..	$16 \times 6 = 96$
VIII.— $1 \times 2 = 2$	..	$32 \times 5 = 160$	..	$16 \times 6 = 96$

Similarly, nitrogen (combining weight 14) forms with oxygen a series of five compounds which exhibit this law in a manner equally striking.

TABLE SHOWING COMPOUNDS OF NITROGEN WITH OXYGEN.

Nitrogen.		Oxygen.
I.— $14 \times 2 = 28$	.. ..	$16 \times 1 = 16$
II.— $14 \times 2 = 28$	.. ..	$16 \times 2 = 32$
III.— $14 \times 2 = 28$	.. ..	$16 \times 3 = 48$
IV.— $14 \times 2 = 28$	.. ..	$16 \times 4 = 64$
V.— $14 \times 2 = 28$	.. ..	$16 \times 5 = 80$

In these tables the horizontal row of figures opposite each Roman numeral represents the composition by weight of one compound. The law here brought to light is known as the *law of multiple proportions*, and from this we are naturally led to the next portion of our subject.

### C.—THE ATOMIC THEORY.<sup>1</sup>

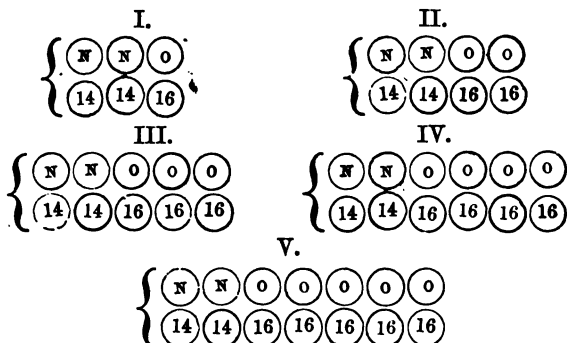
(1) **Elementary Atoms.**—It is a familiar fact that most solid substances can, by mechanical means, be reduced to extremely fine powders; but when this mechanical division is pushed to its utmost limits, the microscope still reveals the particles<sup>2</sup> which compose the powder. How far this division of matter can be carried is a question which has occupied the attention of philosophers for ages. While some have imagined that there is no limit to the divisibility of matter, others have maintained that a point must at length be reached where further division is impossible—where, in fact, we reach the *ultimate* particle. The law of multiple proportions, just explained, was first made clear by our own countryman, Dalton, in 1804. He assumed that matter was composed of such ultimate particles or *atoms*,<sup>3</sup> and, by assigning to the atom of each element a weight corresponding to its combining weight, threw a great flood of light on the obscure law of multiples. On this view of Dalton's a chemical compound is formed by the union of elementary atoms and, as an atom is supposed to be indivisible, we see why, in cases where several compounds of the same elements exist, the increase is always in some multiple of the combining weight. If the atoms of nitrogen and oxygen be represented by the initial letters of these elements, we may thus picture the series of compounds given on p. 9.

<sup>1</sup> *G. theōria*, a speculation.

<sup>2</sup> *L. particula*, a little piece.

<sup>3</sup> *G. α*, not, and *τεμνō*, I cut.

TABLE SHOWING COMPOUNDS OF NITROGEN WITH OXYGEN.



The theory of the existence of atoms, so perfectly in harmony with the law of multiple proportions, is likewise forced upon us by physical considerations into which it is not our province to enter. It is but right, however, here to point out the true position of the atomic theory. That matter behaves both chemically and physically as though built up of small particles is an undeniable fact: whether these particles are the limits of the division possible to matter is neither affirmed nor denied by the theory; neither does the atomic theory assert that the physical particle is identical with the chemical particle. The ancient problem as to whether matter is infinitely divisible or not remains untouched by modern science: it suffices for our purpose to know that these weights are *chemically* indivisible, and we shall therefore be justified in conferring the expression "*atomic weight*" upon those numbers which we have hitherto regarded in the light of combining weights.

Since a study of the several compounds produced by the union of the same elements in different proportions leads us to see that the increase or decrease of any

element in the compound always takes place by the introduction or withdrawal of atoms, we are now enabled to give a more precise definition of this term. The atom is defined by Dr. Frankland as "*the smallest proportion by weight in which the element enters into or is expelled from a chemical compound; the smallest weight of hydrogen so entering or leaving a chemical compound being taken as unity.*"

(2) **Elementary and Compound Molecules.**—We have seen that a chemical compound is produced by the union of elementary atoms; such a combination of atoms forms what is termed a *compound molecule*.<sup>1</sup> While an elementary atom may be briefly defined as the smallest weight of an element that can exist in a chemical compound, an *elementary molecule* may be defined as the smallest weight of an element that can exist in the *free state*. Chemical combination has hitherto been spoken of as occurring between atoms only; in many cases, however, union takes place between molecules; and the combining weight of a molecule, or, in other words, the molecular weight of a compound, is the sum of the combining weights of its constituent atoms. To return again to the series of compounds of nitrogen and oxygen, the molecular weight may be easily found thus:—

Nitrogen.	Oxygen.	Molecular Weight.
I. $(14 \times 2 = 28)$	+ $(16 \quad \quad)$	= 44
II. $(14 \times 2 = 28)$	+ $(16 \times 2 = 32)$	= 60
III. $(14 \times 2 = 28)$	+ $(16 \times 3 = 48)$	= 76
IV. $(14 \times 2 = 28)$	+ $(16 \times 4 = 64)$	= 92
V. $(14 \times 2 = 28)$	+ $(16 \times 5 = 80)$	= 108

In most cases the weight of the elementary molecule is double the weight of the atom; in some cases, however, the weight is the same as that of the atom, while in

<sup>1</sup> L. *molecula*, a little heap; diminutive of *moles*, a mass.

others it is treble or quadruple, and in one case six times the atomic weight. This is equivalent to saying that some elementary molecules consist of one atom, others of two, three, four, or six. The following is a list of the elements whose molecular composition is known<sup>1</sup>:—

*Elements whose molecules consist of One Atom.*

	At. wt.	Mol. wt.
Mercury ..	200 ..	200
Cadmium ..	112 ..	112
Zinc ..	65 ..	65

—of *Two Atoms.*

Hydrogen ..	1 ..	1 × 2 = 2
Oxygen ..	16 ..	16 × 2 = 32
Nitrogen ..	14 ..	14 × 2 = 28
Chlorine ..	35.5 ..	35.5 × 2 = 71
Bromine ..	80 ..	80 × 2 = 160
Iodine ..	127 ..	127 × 2 = 254
Fluorine ..	19 ..	19 × 2 = 38
Sulphur ..	32 ..	32 × 2 = 64
Selenium ..	79 ..	79 × 2 = 158
Potassium ..	39.1 ..	39.1 × 2 = 78.2

—of *Three Atoms.*

Oxygen ..	16 ..	16 × 3 = 48
(modification)		

—of *Four Atoms.*

Phosphorus ..	31 ..	31 × 4 = 124
Arsenic ..	75 ..	75 × 4 = 300

—of *Six Atoms.*

Sulphur ..	32 ..	32 × 6 = 192
(modification)		

(CONTRACTIONS.—“At. wt.” and “Mol. wt.” for “atomic weight” and “molecular weight.”)

<sup>1</sup> The method by which molecular weights are found will be explained when treating of combination by volume.



A solid body, built up of molecules, retains its form and solidity by virtue of a force called *cohesion*,<sup>1</sup> which causes the molecules to attract each other and cling together. This molecular cohesion can be partly overcome by reducing the substance to a powder, but the subdivision is here but imperfect.<sup>2</sup> The application of heat generally causes a more complete separation of the molecules, resulting, first, in a *liquid*, in which the molecules are so far released from the force of cohesion as to glide over and among one another freely; and, finally, in a *vapour*, in which form of matter the molecules, released entirely from the influence of the cohesive force, repel each other. Now, as long as the process of separation is confined to molecules, the substance undergoes no permanent change in properties; when the heat is withdrawn cohesion again comes into play, and the substance gradually assumes its original form: it has undergone only a *physical* change. If, however, the separation is carried beyond the molecular stage; if, by an exercise of "chemical affinity" or of some other force, the *atoms* of a compound molecule are separated, a *permanent* change of properties results: a *chemical decomposition* is said to have taken place. Thus, while molecular division is a *physical* phenomenon, atomic separation is a *chemical* phenomenon; and the student, in thinking over the illustration made use of in the "introduction," will perceive the application of these principles to the familiar substance, water.

#### D.—CHEMICAL NOMENCLATURE.<sup>3</sup>

**Compound Substances.**—The principle upon which some of the simpler compounds are named may be now advantageously introduced to the student's notice.

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<sup>1</sup> L. *cohæro*, to stick together.

<sup>2</sup> The term *molar* (from the same root as molecule) has been applied to this imperfect division in contradistinction to *molecular*.

<sup>3</sup> L. *nomenclatura*, a system of naming.

Compounds of two, three, four, five, six, &c., elements are termed respectively *binary*, *ternary*, *quaternary*, *quinternary*, and *sexternary*<sup>1</sup> compounds.

In binary compounds consisting of a metal and a non-metal, the name of the metal is placed first, and is followed by a word compounded of the name of the non-metal, and ending in *ide*. Thus, copper and sulphur form *copper sulphide*; sodium and chlorine form *sodium chloride*. Generally—

Bromine in combination with metals forms *bromides*.

Carbon	„	„	„	„	<i>carbides.</i>
Chlorine	„	„	„	„	<i>chlorides.</i>
Fluorine	„	„	„	„	<i>fluorides.</i>
Hydrogen	„	„	„	„	<i>hydrides.</i>
Nitrogen	„	„	„	„	<i>nitrides.</i>
Oxygen	„	„	„	„	<i>oxides.</i>
Phosphorus	„	„	„	„	<i>phosphides.</i>
Selenium	„	„	„	„	<i>selenides.</i>
Silicon	„	„	„	„	<i>silicides.</i>
Sulphur	„	„	„	„	<i>sulphides.</i>
Tellurium	„	„	„	„	<i>tellurides.</i>

When a non-metal is capable of combining with a metal or with another non-metal in several proportions, the Greek prefixes, *mono*, *di*, *tri*, *tetra*, *penta*, *hex*, &c., indicate the number of atoms of the non-metal existing in the compound. The compounds of nitrogen with oxygen previously introduced to the student's notice may be now named on this principle by way of illustration.

- I. Two atoms of nitrogen with one atom of oxygen form *nitrogen monoxide*.
- II. Two atoms of nitrogen with two atoms of oxygen form *nitrogen dioxide*.

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<sup>1</sup> From the Latin numerals, *bis*, twice; *ter*, thrice; *quater* four times, &c.

III. Two atoms of nitrogen with three atoms of oxygen form *nitrogen trioxide*.

IV. Two atoms of nitrogen with four atoms of oxygen form *nitrogen tetroxide*.

V. Two atoms of nitrogen with five atoms of oxygen form *nitrogen pentoxide*.

The Greek prefix *per*, signifying *beyond*, is sometimes applied to the compounds containing the largest number of atoms of the metalloïd. Thus :—

One atom of barium with one atom of oxygen forms *barium monoxide*.

One atom of barium with two atoms of oxygen forms *barium peroxide* (or *barium dioxide*).

The Latin prefix *sub*, signifying *under*, is sometimes applied to the compound containing the least number of atoms of the metalloïd. Thus :—

One atom of copper with one atom of oxygen forms *copper monoxide*.

Two atoms of copper with one atom of oxygen form *copper suboxide*.

### E.—CHEMICAL NOTATION.

(1) **Symbols.**—In order to illustrate the law of multiple proportions, we found it convenient to represent the atoms of nitrogen and oxygen by the respective initial letters of the names of these elements, and in so doing we made the first step towards the employment of *chemical symbols*.<sup>1</sup> The symbols now in use are very nearly identical with those introduced by Berzelius in 1815. The symbols of the elements which are given in the table on p. 6, consist merely of the first letter or letters of the English or Latin

<sup>1</sup> G. *sum*, together, and *ballo*, I throw ; meaning a sign.

names of the bodies they represent. By means of this *symbolic notation*,<sup>1</sup> chemists are enabled to express chemical changes much more concisely than by the use of ordinary language.

The symbol of an element always stands for one atom, and consequently for one combining weight of that element. Thus :—

S, O, Cl, N, C, Na, H, Cu, & Sn, stand respectively for 32 parts by weight of sulphur, 16 of oxygen, 35.5 of chlorine, 14 of nitrogen, 12 of carbon, 23 of sodium, 1 of hydrogen, 63.5 of copper, and 118 of tin.

We have seen that the combining weight of a compound is equal to the sum of the combining weights of its constituents; hence, the symbol of a compound is formed by the juxtaposition of the symbols of the elements forming such a compound; HCl, for instance, standing for a molecule of *hydrogen chloride*, having a combining or molecular weight of  $1 + 35.5 = 36.5$ .

When the number of atoms exceeds one, a small figure placed beneath and to the right of the symbol indicates their number. Thus :—

$N_2O$ ,  $N_2O_2$ ,  $N_2O_3$ ,  $N_2O_4$ , and  $N_2O_5$ , stand for nitrogen *mon-, di-, tri-, tetr-, and pent-oxide*, respectively.

When, however, it is wished to indicate that the whole molecule is to be taken more than once, a large figure is placed to the left of the symbol :— $4N_2O_5$ , for example, meaning four molecules of nitrogen pentoxide.

A collection of atomic symbols, representing a compound molecule, is termed a *chemical formula*.<sup>2</sup> The multiplication of whole molecules is sometimes effected by placing the formula in brackets, and treating it as a single atom; thus  $(N_2O_5)_4$  means the same as  $4N_2O_5$ .

<sup>1</sup> L. *notatio*, a description.

<sup>2</sup> L. *formula*, a form.

(2) **Equations.**—The changes which occur when two or more substances act chemically upon one another are represented by placing on the left the formulæ of the substances as they exist *before* the change, connected with each other by the sign +, signifying, as in algebra, addition. On the right are formulated the substances as they exist *after* the change, connected together, as before, by the sign +, and with the remainder of the formulæ by the sign of equality (=). Such a collection of symbols is known as a *chemical equation*; and, as the combining weights of compounds are formed of the sum of the combining weights of their constituents, the numbers on each side of the equation should always be equal. Thus, when sulphur and copper are heated together, we have already stated that chemical combination takes place. This change may be thus expressed as an equation:—



In ordinary language we should say that one atom, or 63.5 parts by weight of copper, unites with one atom, or 32 parts by weight of sulphur, producing 95.5 parts of copper sulphide.

**Summary.**—1. Chemistry is the science which treats of matter, its nature and properties, and the permanent changes produced in it by the action of forces or by the action of other forms of matter. It is organic or inorganic.

2. Matter is either simple or compound: a simple substance is called an element.

3. Chemical affinity is the force which holds together the elements in a compound, and which resists their separation when combined. It acts only at insensible distances.

4. Chemical combination or decomposition produces permanent change of properties in the substances concerned in such combination or decomposition.

5. The elements and their compounds always unite in

the proportion of their combining weights or in some multiple of these numbers.

6. The smallest proportion by weight of an element that can enter into or quit a chemical compound is called an atom. Hydrogen is taken as unity.

7. The smallest proportion by weight of an element that can exist in the free state is termed a molecule; hydrogen being considered as unity.

8. The atoms of the elements are represented by certain signs called symbols; by the juxtaposition of these atomic symbols molecular formulæ are produced.

9. Chemical changes are represented by equations; such equations being always arithmetical identities.

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## NON-METALLIC ELEMENTS AND THEIR COMPOUNDS.

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### CHAPTER II.

#### THE CHEMISTRY OF WATER.

WE may now proceed to apply some of the principles with which we have made ourselves acquainted in the last chapter to some familiar substance; and for this purpose we shall select water.

#### A.—*DECOMPOSITION OF WATER.*

##### I. BY PHYSICAL METHODS.

(a) **By Electricity.**—It has already been mentioned that the force of electricity usually exerts a decomposing influence on compounds submitted to its action. Let the two polar wires from a galvanic battery be

made to terminate in strips of the metal platinum, and let these two platinum plates be dipped into a vessel of water without being allowed to touch each other. We shall observe under these circumstances bubbles of gas rising from each plate through the water. Fig 1 represents a form of apparatus for collecting the gases as they rise.

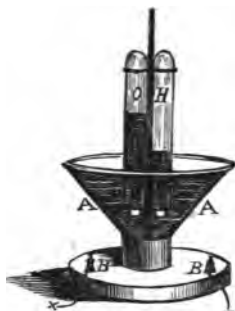


Fig. 1.—Decomposition of water by electricity.

Through the bottom of the conical glass vessel *A* the two wires connected with the platinum plates *rr* are made to pass, and are then connected with the screws *bb*, which enable the wires from the battery (marked + and —) to be put into electrical connection with the platinum plates. The vessel *A* is filled with water (acidulated to make it a conductor), and two tubes (*o* and *h*), which are closed at one end and open at the other, are also filled with water, and inverted in the liquid in the conical vessel *A*, with their open ends downwards. The tubes are supported one over each platinum plate, the water remaining in them by atmospheric pressure on the surface of the water in the conical vessel.<sup>1</sup> On

<sup>1</sup> An arrangement of this kind, known as a *pneumatic trough*, is generally employed for collecting gases. A trough, usually of japanned tin, is fitted with a shelf having a hole through it;

making connection with the battery the bubbles of gas begin to rise and gradually displace the water in the tubes: it will be observed, during the filling of the tubes, that one fills with twice the rapidity of the other.

When a sufficient quantity of gas has been collected in each tube, we may proceed to examine the properties of the gases by closing with the thumb the open end of the tube we wish to examine, removing it from the conical vessel, inverting, and applying a lighted taper to its mouth. When submitted to this test, the gas contained in the tube that had filled the more rapidly will be found to take fire and burn with a pale flame, but the taper itself when pushed into the tube will become extinguished. The gas in the other tube will be found to possess properties exactly opposite to those of the gas first examined: the gas does not take fire, and, instead of putting out the flame of the taper as in the former instance, it will cause it to burn with a dazzling light, and with much greater rapidity than when burning in the air.

We can thus obtain from water, by the action of electricity, two gases of very different properties: one burns in the air, the other does not; one extinguishes the flame of a lighted taper, the other causes the combustion<sup>1</sup> to proceed with greatly increased vigour. The former is said to be *combustible* and a *non-supporter of combustion*, the latter is a *supporter of combustion*, and is *non-combustible*.

---

the vessel to be filled with gas is filled with water, and then placed mouth downwards on the shelf, so that the hole in the shelf corresponds with the centre of the mouth of the vessel. The trough is filled with water to a sufficient extent to cover the shelf, and the tube from which the gas is issuing is placed under the shelf, so that the bubbles rise through the hole up into the vessel to be filled, the water in which is gradually displaced.

<sup>1</sup> *L. combustio*, from *comburo*, to burn.



Water is thus proved, in opposition to the ancient belief, to be a *compound body*, since we can obtain other substances from it. The two substances obtained are the elements *oxygen* and *hydrogen*; oxygen being the gas that supported combustion, hydrogen the one that was combustible.

(b) **By Heat.**—When water in the form of steam is heated to a temperature of about  $1,000^{\circ}\text{C}.$ ,<sup>1</sup> decomposition occurs with the liberation of hydrogen and oxygen. This splitting up of water into its constituents was first accomplished by Mr. Grove, who passed steam through a platinum tube heated to whiteness. The decomposition also occurs when the spark-current from an induction coil<sup>2</sup> is allowed to traverse a tube through which is passing a current of steam.

## II. BY CHEMICAL METHODS.

(c) **By Potassium and Sodium.**—The decomposition of water by physical methods leads, as we have seen, to the liberation of both its constituents. When, however, we act upon water with a substance capable of effecting its decomposition only one element is set free, the other combining with the substance employed. Thus the two metals potassium and sodium possess such a strong affinity for oxygen that they are capable of liberating hydrogen from its combination with this element. A fragment of potassium thrown on to the surface of water rolls about with a hissing sound, and becomes so hot, from the energy of the chemical action going on, as to ignite the liberated hydrogen, which burns with a beautiful violet-coloured flame.<sup>3</sup> Sodium

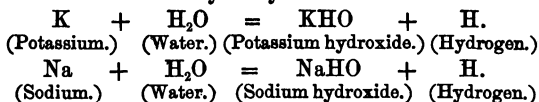
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<sup>1</sup> Meaning 1,000 degrees centigrade. See Appendix I.

<sup>2</sup> For particulars on the subject of the induction coil the student should consult some work on electricity.

<sup>3</sup> Hydrogen itself burns with a nearly colourless flame; the colour is here due to the volatilisation of potassium compounds, which, as we shall see hereafter, give a violet colour when

behaves in a similar manner to potassium, except that the hydrogen does not take fire unless the water be warm or unless the globule be retarded in its motions by a piece of blotting paper. The water on which the experiment has been made will be afterwards found to contain in solution a substance consisting of the metal used, combined with hydrogen and oxygen—otherwise a *hydroxide*. The changes occurring by the action of the metal on water may be symbolised as follows:—



The student will here perceive the mode of applying *chemical equations*.

If, instead of allowing the hydrogen to take fire in these experiments, we push the fragment of metal down under the water by means of a spoon made of wire gauze, the gas will rise in bubbles through the water, and may be collected by the “pneumatic trough” arrangement described when treating of the decomposition of water by an electric current. Fig. 2 shows the general disposition of the apparatus.



Fig. 2.—Decomposition of water by potassium or sodium.

made to glow in the vaporous state. For a similar reason the flame of burning sodium is bright yellow.

Pieces of metal, each about the size of a pea, are thrown on to the surface of the water, and then immediately conveyed under the mouth of the jar to be filled, which, in a short time, has its water displaced by hydrogen.

Under whatever physical conditions a substance may occur, it is to the chemist unaltered as regards its composition. Thus, water is composed of hydrogen and oxygen, whether it is in the solid form as ice, in the liquid form as water, or in the vaporous condition as steam. The decomposition above described is effected, therefore, by the metals potassium and sodium, in whatever physical state the water is presented to them. A fragment of either of these metals placed on a block of ice immediately becomes very hot, sinking down with great rapidity into a self-excavated hollow, from which the globule of molten hydroxide is sometimes forcibly ejected. So, also, steam, when passed over potassium or sodium, undergoes decomposition with the liberation of its hydrogen.

(d) **By Iron.**—We have just seen that potassium and sodium effect the abstraction<sup>1</sup> of oxygen from water at ordinary temperatures; there are many other metals which effect the decomposition only when raised to a high temperature. Thus, iron decomposes water when the metal is heated to redness, and the water is passed over it in the form of steam. Under these circumstances the oxygen combines with the iron to form an *oxide* composed of 3 atoms of iron to 4 of oxygen, and named therefore, in accordance with the system briefly indicated in the last chapter, *triferrous tetroxide*. The reaction<sup>2</sup> may be thus expressed in symbols:—

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<sup>1</sup> *L. abstraho*, meaning the withdrawal.

<sup>2</sup> When chemical change occurs between any substances brought together, these are said to *react* upon one another, and the change is said to be a *reaction*. (*L. re* and *ago*.)



In Fig. 3 we have represented the arrangement of the apparatus for producing this decomposition.

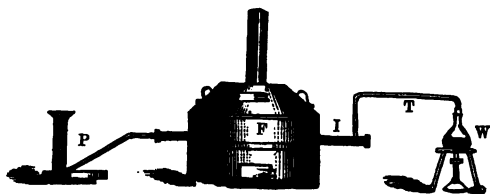
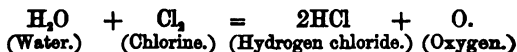


Fig. 3.—Decomposition of water by red-hot iron.

The flask containing water is seen to the right at W on a tripod stand over a gas flame. The steam rising from the boiling water passes through the glass tube T into the iron tube I, which is placed in the furnace F, and thus heated to redness through its entire length. The iron tube may conveniently consist of a piece of iron gas-piping, and should be filled up with nails or iron turnings. The arrangement for collecting the hydrogen is seen to the left at P, and consists of the pneumatic trough already used on former occasions.

(e) **By Chlorine.**—In the foregoing cases the decomposition of water has been effected by withdrawing the oxygen. It is also possible to decompose water by acting on it with an element having a powerful affinity for its hydrogen. Such an element is *chlorine* (see table of elements, p. 6), and when a mixture of this gas with steam is passed through a red-hot tube, the chlorine combines with the hydrogen, forming a compound which, in accordance with the rules of nomenclature previously laid down (p. 15), is termed *hydrogen chloride*, the oxygen being set free. This reaction is thus expressed symbolically:—



The apparatus for conducting this experiment is very similar to that shown in Fig. 3; a flask generating chlorine being interposed between the steam-generating flask and the iron tube, which for the present experiment is replaced by an empty porcelain tube. The method of obtaining chlorine will be considered hereafter.

### B.—QUANTITATIVE COMPOSITION OF WATER.

**Definitions.**—When a compound substance is by any process split up into its constituent elements, we are said to make an *analysis*<sup>1</sup> of such a compound. When, conversely, a compound substance is built up from its constituent elements, we are said to make a *synthesis*<sup>2</sup> of such a substance. When an analysis is performed with a view of ascertaining the exact weights of the elements forming a compound, it is said to be a *quantitative analysis*. When, however, it is only the nature of the component elements that we wish to ascertain, the analysis is said to be *qualitative*. We have described many cases in which water has been submitted to qualitative analysis in the foregoing pages; we have now to consider its composition from a quantitative point of view; we have to make ourselves acquainted with the practical methods by which the formula  $\text{H}_2\text{O}$ , assigned to the water molecule in the previous reactions, has been obtained.

(a) **By Synthesis.**—The simplest method of ascertaining the quantitative composition of water is a method of synthesis. When a stream of hydrogen gas is passed over *copper monoxide* heated to redness, this substance gives up all its oxygen to the hydrogen to produce

<sup>1</sup> G. *ana*, again, and *luō*, I liberate.

<sup>2</sup> G. *sun*, together, and *tithēmi*, I put.

water, while metallic copper is left behind. It is plain that it would be only necessary to know the weight of the oxygen used and the weight of the water produced, to have all the data<sup>1</sup> for the required calculation.

The method of performing the experiment is shown in Fig. 4.

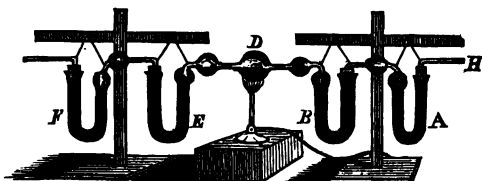


Fig. 4.—Quantitative synthesis of water.

The hydrogen gas enters through the tube H, and passes through the U-shaped tubes A and B, which contain some substance having a strong affinity for water,<sup>2</sup> so that the gas is perfectly dry when it reaches the bulb-tube D. In the bulb-tube D is placed the copper monoxide, which is heated during the experiment by a gas flame. The water produced passes as steam into the U-tubes E and F, which also contain some of the water-absorbing substance. Before the experiment is started, the bulb-tube D, with its oxide of copper, is accurately weighed; so, also, are the U-tubes E and F, with their contained absorbent. After passing the hydrogen through the apparatus, till the copper monoxide is all reduced to the metallic state, the bulb-tubes and U-tubes are again weighed. The loss of weight in the bulb-tube represents the quantity of oxygen used; the gain of weight in the U-tubes represents the

<sup>1</sup> *L. do, datum.* The elements given for a computation.

<sup>2</sup> For this purpose dried calcium chloride, phosphorus pent-oxide, or fragments of pumice-stone moistened with oil of vitriol may be used.

amount of water formed. As hydrogen and oxygen are the sole constituents of water, it is obvious that the amount of oxygen used subtracted from the weight of water produced gives the quantity of hydrogen in that amount of water. The results of such a synthesis are shown below :—

						Grammes.
Weight of bulb-tube and cop. oxide before heating,						60.50
"	"	"	"	after	"	58.50
						<hr/>
"	oxygen used	..	..	..	..	2.00
						<hr/>
"	U-tubes after heating bulb	..	..	..	..	70.25
"	" before	"	..	..	..	68.00
						<hr/>
"	water produced	..	..	..	..	2.25
						<hr/>
"	"	"	..	..	..	2.25
"	oxygen used	..	..	..	..	2.00
						<hr/>
"	hydrogen used	..	..	..	..	0.25
						<hr/>

We thus learn that in 2.25 parts of water there are two parts of oxygen and 0.25 parts of hydrogen. We may express this result for 100 parts as follows :—

$$2 : 0.25 = 88.89 : 11.11.$$

In water, therefore, the quantity of oxygen is to the quantity of hydrogen as 8 : 1; since  $2 : 0.25 = 8 : 1$ . But we have assigned to oxygen the combining weight 16; hence one combining unit or atom of oxygen requires two atoms of hydrogen, and the formula is consequently  $H_2O$ .

Confirmation of the previous result may be obtained by making a mixture of hydrogen and oxygen in the proportions above indicated, and exploding them in a confined vessel. The method of performing the experiment is shown in Fig. 5.

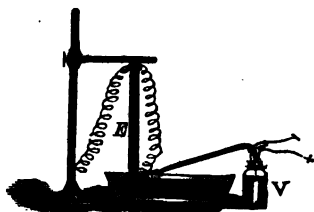


Fig. 5.—Eudiometrical synthesis of water.

E is a strong glass tube sealed up at one end and open at the other. Into the sealed end two platinum wires are fused so as nearly to touch inside the tube.<sup>1</sup> V is a bottle with a cork fitted to it. Through the cork pass the bent glass tube *t* and the two wires + and —, which are connected with two platinum plates inside the bottle. Water (acidulated with a few drops of oil of vitriol) is poured into the bottle, and the two wires + and — being connected with a battery, the mixed gases pass out through the bent tube, and may be collected in the tube E by the ordinary pneumatic trough arrangement, only in this case the trough T and the tube E are filled with mercury instead of water. When the tube is about half full of the mixed gases, its mouth is firmly pressed down on to a piece of india-rubber beneath the mercury at the bottom of the trough, and an electric spark is then passed between the two platinum wires. The gases combine with a bright flash, and the inside of the tube becomes covered with a film of moisture—the water produced by the combination of the gases. On raising the tube from the india-rubber cushion, the mercury rises and completely fills it, showing that a vacuum exists, owing to the dis-

<sup>1</sup> This tube is known as a *eudiometer*. (G. *ēudios*, purity of air, and *mētrōn*, a measure.) So called because this instrument is used, as we shall see hereafter, to analyse the atmospheric air.



appearance of the gases, and thereby proving that oxygen and hydrogen are the sole constituents of water. The composition of water by synthesis was first shown by Cavendish in 1781.

### C.—DISTRIBUTION AND PROPERTIES OF WATER.

**Distribution.**—Water is a substance most abundantly distributed in nature—nearly two-thirds of the earth's surface being covered by it. It enters into the composition of most animal and vegetable substances, and is a constituent of many minerals. In the form of vapour it is always present in the atmosphere, while as snow it always covers the tops of the highest mountains, and as ice it forms vast fields in the polar regions.

**Properties.**—Water between the temperatures of  $0^{\circ}$  and  $100^{\circ}$  C. is a tasteless, inodorous liquid, transparent and colourless when seen in small depths, but of a bluish-green when viewed in great depths. At a temperature of  $0^{\circ}$  C. ( $32^{\circ}$  Fahrenheit) water solidifies to ice, which is a crystalline, transparent substance of a slightly greenish-blue tint when seen in great thicknesses. In passing from the liquid to the solid state, water expands by nearly one eleventh of its volume—that is to say, one volume of water becomes  $1\frac{1}{11}$  volumes of ice. The force of this expansion is almost irresistible; a strong iron bottle filled with water and frozen is burst into fragments by its power. The bursting of water-pipes during a frost is due to this expansion of water when freezing. Since ice occupies more space than the water from which it is produced, it follows that ice is lighter than water; its *specific gravity*<sup>1</sup>—that is, its weight compared with the

<sup>1</sup> For the methods of determining the specific gravity of bodies, see "Mechanics" in this series.

weight of an equal volume of water—is 0.92, the weight of the volume of water being 1. At all temperatures water is evaporating;<sup>1</sup> even ice and snow gradually disappear by evaporation. Under the ordinary atmospheric pressure, at a temperature of 100° C. water *enters into ebullition*<sup>2</sup> (or boils) and becomes converted into steam, which is a transparent and colourless vapour. The white cloud seen escaping from boiling water is not true steam, but minute particles of water suspended in the air and produced by the condensation<sup>3</sup> of the true steam. In passing from the liquid to the vaporous condition water undergoes enormous expansion, one volume of water at 0° becoming 1698 volumes of steam at 100°. The boiling point of water is much lowered when the pressure of the atmosphere is reduced. Conversely, the boiling point is raised when the atmospheric pressure is increased. Thus, *in vacuo* water may be made to boil at nearly 0° C., while under a pressure of 45 atmospheres the temperature is raised to 266° C. Water is 770 times heavier than an equal bulk of atmospheric air, steam having a specific gravity of 0.622 at 100° C. when compared with an equal bulk of air at the same temperature. When water is heated from 0° C., it contracts till the temperature reaches 4° C.; beyond this point it goes on expanding. On either side of 4° C., then, water is lighter than at 4° C.; hence this point is called the point of *maximum density* of water. The weight of one *cubic centimetre*<sup>4</sup> of water at the maximum density is the unit weight of the French system of weights. It is called the *gramme*, and is equal to 15.432 grains. One cubic foot of water weighs 1,000 ounces, and one gallon weighs 10 lbs.

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<sup>1</sup> L. *evaporo*, to disperse in vapour.

<sup>2</sup> L. *ebullio*, to boil.

<sup>3</sup> L. *condenso*, to make thick.

<sup>4</sup> The French system of weights and measures will be used throughout this book. See Appendix II.

Many solid substances are capable of dissolving in water, the degree of solubility varying for each substance. In general hot water dissolves more of a substance than cold water; but there are marked exceptions to this rule. Water also dissolves many gases, the amount dissolved depending to a large extent on the pressure. With gases, the amount dissolved becomes smaller the higher the temperature of the water.

**Distillation.**—Water never occurs in a state of purity in nature, as it always contains some substances in solution, either gaseous or mineral, or both. Rain is the purest form under which water occurs in nature; but even this is to a certain extent contaminated by dissolved impurities. Water may be freed entirely from solid impurities by boiling it in a vessel constructed so as to permit the steam to be condensed as it escapes. Such a vessel is shown in Fig. 6, and is called a *retort*. This process of purification is termed *distillation*.<sup>1</sup>

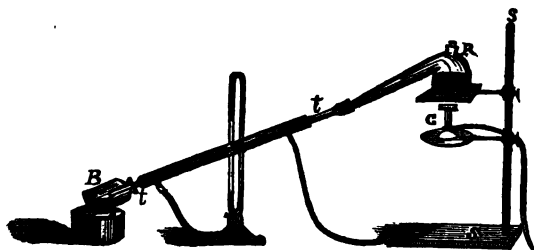


Fig. 6.—Distillation of water.

The water is boiled in the retort *R* by being placed over the gas burner *e*; it is most conveniently supported in this position by being placed on a sheet of wire gauze resting on the sliding ring of the stand *ss*,

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<sup>1</sup> *L. distillo*, to drop a little by little.

called a *retort stand*. The steam passes down the neck of the retort into a tube ( $t$ ), which is kept cool by being surrounded by a wider tube, through which a current of cold water is circulating. This condensing apparatus is known as "Liebig's condenser." The condensed steam flows as water down the inner tube  $t$  into the bottle  $B$ , placed to receive it. For distilling on a large scale a metal vessel called a *still* is employed, and the steam is condensed by passing through a spiral tube placed in a tub of water kept cool by circulation.

**Latent Heat.**—A thermometer plunged into melting ice indicates a temperature of  $0^{\circ}\text{C}$ ., and this temperature remains constant as long as there remains a fragment of solid ice in the liquid. Now it is obvious that during the melting of the ice heat is being imparted to the vessel and its contents—yet the thermometer does not begin to rise till the last particle of ice is liquefied. The heat thus made to disappear during the liquefaction of ice is said to be *latent*.<sup>1</sup> It is in reality used up in doing the work of separating the molecules of the solid. The latent heat of water is 79—that is to say, the amount of heat which would cause a given weight of ice to become liquid would raise the temperature of an equal weight of water through  $79^{\circ}\text{C}$ . A similar disappearance of heat takes place when water passes into the state of vapour. A vessel of water, with a thermometer plunged into it, continues to rise in temperature when placed over a source of heat till the water boils; when the thermometer remains constant, under the ordinary atmospheric pressure, at  $100^{\circ}\text{C}$ . The heat here absorbed is also said to be rendered latent, and

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<sup>1</sup> "Latent heat is the quantity of heat which must be communicated to a body in a given state in order to convert it into another state without changing its temperature."—*J. Clerk Maxwell*. For further particulars on latent heat, and on the methods of its determination, the student should refer to the volume on Heat in this series.

is used up in doing the work of molecular separation. The latent heat of steam is 536.

**Specific Heat.**—Different substances absorb different amounts of heat in rising through equal temperatures: this *capacity for heat*, when referred to some substance having a large capacity for heat as unity, is the *specific heat*<sup>1</sup> of a substance. Water, having a very large capacity for heat, is made unity in these determinations. The physical properties of water have a most important bearing in the economy of nature. The formation of dew and rain, of snow and hail, can be explained when we know these physical properties. The great specific and latent heat of water, as well as its wonderful property of *contracting*, when heated from 0° to 4° C., play a very important part in nature's processes; but we cannot here give space to these subjects, as they belong properly to the science of Physics as applied to Physical Geography.

The mineral substances held in solution by most natural waters will be considered when we have acquired a greater familiarity with these substances in subsequent chapters. Let us now, therefore, pass on to the consideration of the elements hydrogen and oxygen, which, as we have just learnt, compose water.

## 1. HYDROGEN.<sup>2</sup>

Symbol, H. Atomic weight, 1.

**Occurrence.**—Hydrogen rarely occurs in a free state in nature. It forms  $\frac{1}{8}$  by weight of the water existing on the globe, and this is consequently its most abundant

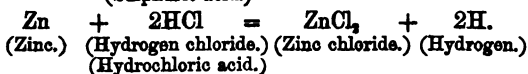
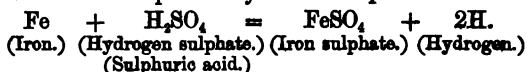
<sup>1</sup> "The specific heat of a body is the ratio of the quantity of heat required to raise that body one degree to the quantity required to raise an equal weight of water one degree."—*J. Clerk Maxwell*. The remarks in the last foot-note are equally applicable here.

<sup>2</sup> G. *hudōr*, water, *gēnnaō*, I produce. The student will at once perceive the applicability of this term.

source. Hydrogen enters into the composition of all animal and vegetable tissues, and has been found in certain specimens of meteoric iron. This gas has been found by optical methods of research<sup>1</sup> to exist in the atmosphere of the sun and some of the fixed stars.

**Preparation.**—Many methods of preparing hydrogen were given when considering the decomposition of water; these methods, therefore, need not again detain us.

Hydrogen is most conveniently prepared by acting on the metals zinc or iron, either with hydrochloric acid (HCl) or with sulphuric acid (H<sub>2</sub>SO<sub>4</sub>). The reactions that take place may be thus expressed:—



The apparatus for preparing the gas is shown in the annexed figure.

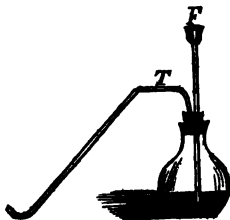


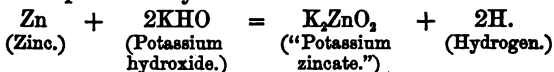
Fig. 7.—Hydrogen-generating flask.

A flask or wide-mouthed bottle has a cork tightly fitted into its neck. This cork is perforated by two

<sup>1</sup> Reference is here made to *spectrum analysis*, for further details of which our treatise on Light may be consulted.

holes, through one of which passes the tube *r*, terminating in its upper end in a funnel, while its lower extremity passes down to nearly the bottom of the flask. The other hole of the cork has the bent tube *r* passing through it. This tube only just passes through the cork, and does not extend for any distance into the flask. Zinc or iron scraps being placed in the flask, the acid diluted with water (eight times in the case of sulphuric, twice in the case of hydrochloric) is poured down the funnel-tube. A brisk effervescence<sup>1</sup> soon sets in, and the gas escapes through the bent tube, since the end of the funnel-tube is under the liquid. As soon as all the air has been driven out of the flask, the gas may be collected for examination over the pneumatic trough.

Hydrogen is also formed when potassium or sodium hydroxide is boiled with zinc and water. This process is not a very convenient one for practical purposes, as the mixture froths very much. A flask similar to that shown in Fig. 7 may be used. The reaction may be thus expressed in symbols:—



**Properties.**—Hydrogen is a colourless and transparent gas, possessing, when pure, neither taste nor smell: it is the lightest body known, being  $14\frac{1}{2}$  times lighter than atmospheric air. Owing to this low specific gravity, hydrogen may be collected without the use of the pneumatic trough; it is only necessary for this purpose to connect a straight tube with the generating flask, and to push this tube up to the top of an inverted jar. The gas as it fills the vessel displaces the heavier air. For a similar reason, hydrogen gas escapes rapidly from a vessel with its mouth upwards, while it is retained for a longer time in a vessel with its mouth

<sup>1</sup> *L. effervescentia*, a sudden boiling.

downwards: the gas can, indeed, be poured upwards from one vessel into another, as shown in Fig. 8.

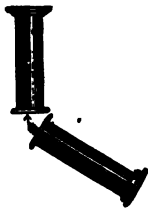


Fig. 8.—Upward decantation of hydrogen.

Hydrogen gas, as we have already seen, does not support combustion, but is itself combustible, burning in the air with a pale flame which gives very little light but is intensely hot. The product of this combustion is water: a cold glass vessel held over a hydrogen flame becomes immediately covered with a film of water, which soon collects into drops and trickles down the sides of the vessel. When mixed with air or oxygen, hydrogen gas explodes with violence on the application of a lighted taper—the product of the combination being water, as in the case of the eudiometrical synthesis previously described. It is on account of this explosive property that it is necessary in dealing with hydrogen to wait till all the air has been expelled from the generating vessel, which might otherwise be shattered by incautiously igniting the gas. Hydrogen and oxygen may be burnt together from a jet of special construction. The safest form for the *oxy-hydrogen blowpipe* is that of a jet of burning hydrogen, through the centre of which the oxygen is blown from a jet of small aperture. The flame is not luminous, but is intensely hot, melting the most refractory substances, such as platinum and quartz, and causing a piece of lime to glow with an intense light, known as the “lime light.”



Hydrogen has not been reduced to the liquid state by the greatest pressure and cold to which it has been submitted.

In its general chemical properties hydrogen behaves much like certain metallic elements, and it has been found by Professor Graham that the metal palladium absorbs an immense quantity of this gas, amounting under certain conditions to 982 times its volume. This *palladium hydride* possesses many of the characteristics of a true alloy,<sup>1</sup> and hydrogen gas has been therefore considered a highly volatile<sup>2</sup> metal, termed *hydrogenium*.

Hydrogen, being the lightest known substance, and having the lowest combining weight of all the elements, is made the unit of the present system of atomic weights. This gas was known so far back as the sixteenth century, but Cavendish, in 1766, was the first to study its properties with any degree of exactness.

## 2. OXYGEN.<sup>3</sup>

Symbol, O. Atomic weight, 16.

**Occurrence.**—Oxygen forms  $\frac{8}{8}$  by weight of water, and  $\frac{2}{2}$  of the air: it enters into the composition of all animal and vegetable tissues, and forms about half by weight of the solid earth: so that oxygen is the most abundant of the elements.

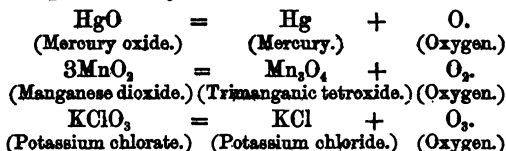
**Preparation.**—Oxygen is generally prepared by heating some decomposable substance containing this element. The materials most commonly employed are

<sup>1</sup> A combination of two metals is termed an *alloy*. From certain considerations concerning the specific heat of hydrogen, it has been recently inferred that the combination of hydrogen with palladium is not a definite chemical compound; the term *palladium hydride* is not, therefore, strictly applicable.

<sup>2</sup> L. *volare*, to fly; meaning, to go off readily into vapour.

<sup>3</sup> G. *oxus*, an acid, and *gemma*, I produce. So called because this element was formerly considered an essential constituent of all acids.

mercury oxide ( $\text{HgO}$ ), manganese dioxide ( $\text{MnO}_2$ ), or potassium chlorate ( $\text{KClO}_3$ ). The changes that occur when these substances are decomposed by heat may be expressed in symbols as follows:—



Potassium chlorate is the substance most frequently used, as it gives off its oxygen at a moderate temperature, and yields about 39 per cent. of its weight of the gas. Although potassium chlorate gives off oxygen when heated by itself, the decomposition occurs at a much lower temperature if some other substance, unacted upon by oxygen, is mixed with it. For this purpose iron rust or manganese dioxide may be used.

The material thus mixed with the chlorate undergoes no change itself, but appears to act merely by its presence—the exact cause of this peculiar action being not yet understood.

A convenient piece of apparatus for preparing oxygen from potassium chlorate (mixed with manganese dioxide or some other substance) may be made by fitting a cork and bent tube to a glass oil flask, as shown in Fig. 9.



Fig. 9.—Flask for preparing oxygen.

The mixture is introduced into the flask, and then heated gently over a gas flame: the oxygen passes out

through the bent tube, and may be collected at the pneumatic trough.

Many other processes yield oxygen, but we cannot here devote space to their consideration. Its preparation from water has been already considered, so that we may now pass on to the properties of the gas.

**Properties.**—Oxygen, like hydrogen, is a colourless, transparent, inodorous, and tasteless gas, not reducible to the liquid state by any known pressure or degree of cold. It is slightly heavier than the atmospheric air, and sixteen times heavier than hydrogen when equal bulks of these gases are compared at the same temperature and pressure. Oxygen is slightly soluble in water, 100 volumes of water dissolving about three volumes of the gas at the ordinary temperature of the air.

Although not itself combustible, oxygen is a most energetic supporter of combustion, substances that burn in the air burning with much-increased energy in oxygen gas. Charcoal, sulphur, and phosphorus, when burnt in oxygen, form most brilliant spectacles; and the metals iron and zinc can be made to burn readily in the gas. We have already had occasion to mention that oxygen supports the combustion of hydrogen to an explosive degree when these two gases are mixed and fired. The opportunity here presents itself for proving that the terms *combustible* and *supporter of combustion* are entirely relative. A jet of hydrogen, for example, burns in the air or in oxygen: here we say the hydrogen is the combustible and the air the supporter of the combustion. But the converse obtains, for we may plunge a jet of oxygen into burning hydrogen, when a flame attaches itself to the oxygen jet, which thus burns in the hydrogen: here the oxygen is the combustible and the hydrogen the supporter of the combustion. Fig. 10 shows the manner of conducting the experiment.

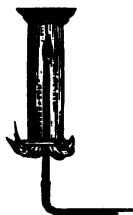


Fig. 10.—Combustion of oxygen in hydrogen.

The jar of hydrogen is inverted, and the gas kindled at its mouth; the jet, connected with a bladder or bag of oxygen, is then pushed through the hydrogen flame up into the jar, when the oxygen ignites as above described.

The energy with which oxygen supports combustion is such that a wooden splint with only a glowing spark is immediately rekindled on being plunged into the gas.

Oxygen was discovered in 1774 by Priestly, and, independently, in 1775 by Scheele.

**Ozone.**—When oxygen gas is electrified by the passage of a “brush discharge” through it, it undergoes condensation, acquires a peculiar odour, and becomes much more active than ordinary oxygen. In this condition it combines with many metals at ordinary temperatures, and liberates iodine from its combination with potassium (potassium iodide, KI). This modified oxygen is termed *ozone*,<sup>1</sup> and is regarded as oxygen having three atoms to the molecule ( $O_3$ ), ordinary oxygen being a diatomic molecule ( $O_2$ ). Ozone exists in small traces in the atmosphere.

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<sup>1</sup> G. *ozein*, to emit a smell.

**Summary.**—1. Water is a compound substance composed of the elements hydrogen and oxygen united in the proportion of 2 : 16.

2. Water may be resolved into its elements by the action of heat and of electricity.

3. The hydrogen may be liberated by the action of potassium, sodium, and iron; the oxygen by the action of chlorine.

4. When a compound is split up into its constituent elements an *analysis* is performed.

5. When a compound is built up from its constituent elements a *synthesis* is performed.

6. Analysis and synthesis may be *qualitative* or *quantitative*.

7. Hydrogen is generally prepared by acting with sulphuric acid and water on zinc or iron.

8. Oxygen is generally prepared by heating potassium chlorate mixed with manganese dioxide.

9. When oxygen is electrified it contracts in volume, becomes more active, and acquires a peculiar odour. In this state it is known as *ozone*.

10. The molecule of ozone contains three atoms, the molecule of ordinary oxygen being diatomic.

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## CHAPTER III.

## CHEMISTRY OF THE ATMOSPHERE.

## A.—PHYSICAL PROPERTIES.

THE aërial ocean, or *atmosphere*,<sup>1</sup> in which we live envelopes the globe, and exerts a pressure upon its surface of 14.7 lbs. on each square inch. The reason why this great weight of air is not felt by us is, because the pressure is exerted equally in every direction, so that the pressure of the air within our bodies balances the pressure of that without. All gases possess the property of *elasticity*—that is, they are capable of being condensed by pressure, and return to their former bulk when the pressure is removed. Owing to this elasticity the air decreases in density as we ascend from the earth's surface, because the higher any layer of the atmosphere is situated, the less will be the pressure to which it is subjected by the weight of the superincumbent<sup>2</sup> air. Thus, at an elevation of about  $3\frac{1}{2}$  miles the density of the air is one-half of its density at the earth's surface, while at an elevation of about 7 miles its density is only one-fourth of this quantity. The height to which the atmosphere extends above the sea-level is generally estimated at about 45 miles. The pressure of the air may be shown and measured by means of an instrument called a *barometer*.<sup>3</sup> In treating of the pneumatic trough (see p. 20), we have already seen how a bottle

<sup>1</sup> G. *atmós*, air; *sphaira*, a sphere.

<sup>2</sup> L. *super*, upon; *incumbens*, lying.

<sup>3</sup> G. *barós*, weight; *métrōn*, a measure.

filled with water and inverted in a vessel of water remains filled with the liquid, and it was then stated that the pressure of the atmosphere maintains the water in this position. In such an arrangement we have what may be called an incipient barometer. A perfect barometer is formed when for the bottle we substitute a glass tube, about 800 millimetres long, and sealed at its upper end; this tube being filled with mercury, and inverted in a vessel of the same liquid, as shown in the accompanying figure.



Fig. 11.—Barometer tube.

Now the pressure of the atmosphere on the surface of the mercury in the vessel A is, as already stated, 14.7 lbs. on the square inch: the column of mercury in the tube B, therefore, sinks until the weight of the column of mercury equals this pressure; that is, until equilibrium is reached.<sup>1</sup> Under ordinary circumstances the height of mercury thus supported is about 760 millimetres—the remaining space being vacuous. A barometer indicates variation in atmospheric pressure by the rising and sinking of the mercurial column.

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<sup>1</sup> For further particulars our volume on Hydrostatics may be consulted.

Were water used instead of mercury, a column of 10.29 metres would be required. As the pressure of the air decreases as we rise from the earth's surface, the mercury column of a barometer sinks in ascending a mountain; so that this instrument is used for measuring heights.

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### B.—CHEMICAL COMPOSITION.

(a) **Qualitative Composition.**—If atmospheric air be passed over metallic copper heated to redness and then collected at the pneumatic trough, we shall find that it undergoes a marked change in properties. The same apparatus may be used as that employed for decomposing water by red-hot iron (see p. 25), a glass tube filled with copper turnings replacing the iron tube, and a bag filled with air being substituted for the flask of boiling water. During the course of such an experiment the bright surface of the copper becomes blackened, and the gas collected may be examined in the usual way by a lighted taper. This gas neither burns nor supports combustion. It is the element *nitrogen*, which we have thus proved to enter into the composition of the atmosphere. The blackening of the copper is due to the formation of *copper monoxide*, as may be proved by passing hydrogen through the heated tube, when water will be formed and the bright surface of the copper restored. We thus prove that *oxygen* is also a constituent of the atmosphere.

(b) **Quantitative Volumetric Composition.**—By burning some substance having a strong affinity for oxygen in a confined portion of air we can remove the whole of this constituent. For this purpose *phosphorus*—a substance whose properties will be described hereafter—may be employed. The method of conducting the experiment is shown in Fig. 12.





Fig. 12.—Removal of oxygen from air by burning phosphorus.

A piece of phosphorus is floated in a small dish on the surface of a vessel of water, and after ignition by means of a hot wire an empty jar divided into five equal portions by means of india-rubber rings is inverted over the dish and its burning contents. The phosphorus unites with the oxygen to form *phosphorus pentoxide*, thus :—



This substance is given off in white flakes, which ultimately dissolve in the water. After the phosphorus has ceased burning, the vessel must be allowed to remain undisturbed for about half an hour, by which time the phosphorus pentoxide will be all dissolved and the contents of the vessel cooled down. The water will then be found to have risen in the jar to the extent of one of the divisions, and the residual gas will be found on examination to be nitrogen. We thus prove that volumetrically the air is composed of nitrogen and oxygen, mixed in the proportion of about 4 to 1, or, in 100 parts—

Nitrogen .....	79
Oxygen .....	21
	<hr/>
	100
	<hr/>

Further confirmation of this result may be obtained by burning a known quantity of air in a *eudiometer* with hydrogen. For this purpose a certain quantity of

air is passed up into the eudiometer (see Fig. 5, p. 29) and its volume read off; an excess of hydrogen is now added, and the volume again read off. The mouth of the eudiometer is then firmly pressed down upon a sheet of india-rubber under the mercury in the trough, and an electric spark passed between the wires. An explosion occurs, and on raising the eudiometer from its india-rubber cushion the mercury rises in the tube and occupies a certain number of divisions. This contraction of the contained gases is due to the removal of the whole of the oxygen contained in the air in combination with hydrogen as water. The water produced occupies such a minute space that its volume may be neglected. We may now recall to the student's memory the fact observed when treating of the quantitative analysis of water. (See p. 28.) It was then found that the *volume* of hydrogen produced was double the volume of oxygen; in other words, water is composed of two volumes of hydrogen to one of oxygen. Since one volume of oxygen, then, combines with two volumes of hydrogen, one-third of the contraction above described is due to oxygen. We have thus all the data necessary for a calculation, as the following example will serve to illustrate:—

					Cubic centimetres.
Volume of air introduced into eudiometer ..					200
„ hydrogen „ „ ..					100
Total volume of mixed gases before explosion					300
„ „ „ after „ ..					174
Contraction ..					126
Cubic centimetres.					
Oxygen contained in 200	=	$1\frac{2}{3}$	=	42	
That is, in .. 100	=	$\frac{4}{3}$	=	21	

(c) **Quantitative Composition by Weight.**—The composition of the atmosphere *by weight* can be ascertained by passing air through a weighed tube containing red-hot copper into an exhausted and weighed glass globe. The air must for this purpose be freed from all impurities. The increase of weight in the tube containing the copper represents the amount of oxygen mixed with the weight of nitrogen found in the glass globe, and thus the ratio in which these two gases are mixed can be found. The air is by this means found to consist, in 100 parts by weight, of 79 parts nitrogen and 23 parts of oxygen.

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### C.—CHEMICAL PROPERTIES.

It must be understood that the ingredients of the atmosphere are only *mixed* together, and are not, like the oxygen and hydrogen in water, *chemically combined*. In chemical properties, then, the air presents characters nearly intermediate between those of its constituents. Oxygen is, as we have already seen, a most energetic supporter of combustion, while nitrogen does not support combustion.<sup>1</sup> The air is thus a supporter of combustion, owing to its contained oxygen: the nitrogen serves to dilute the intense chemical activity of this latter gas. Air is, as we all know, necessary for the maintenance of life, both animal and vegetable. In the case of animals, it is oxygen that is required: nitrogen alone is fatal to animal life;<sup>2</sup> while in undiluted oxygen the vital activities are increased to an unnatural extent. Oxygen is neces-

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<sup>1</sup> Certain exceptions to this statement occur in the case of one or two very rare metals.

<sup>2</sup> Hence this gas is also sometimes termed *azote*, from the Greek  $\alpha$ , without; *zoe*, life.

sary for respiration, in order to remove the waste products of the blood, and to maintain the temperature of the body above that of the surrounding air. This animal heat is the result of a true combustion or burning—the waste substances of the blood being oxidised<sup>1</sup> into substances of simpler composition; and the heat thus produced is distributed to all parts of the body by means of the circulatory system. Of the substances produced by this oxidation the most hurtful is *carbon dioxide* ( $\text{CO}_2$ ); so that in respiration the removal of this substance is constantly going on. We shall, however, be better qualified to study the chemical changes accompanying respiration when we have acquainted ourselves with the properties of carbon dioxide.

Oxygen and nitrogen are both soluble in water to a very small extent, but oxygen is the more soluble of the two. When, therefore, air is shaken up with water these two gases dissolve in unequal proportions, and the composition of the air driven from water by boiling, compared with ordinary atmospheric air, is as follows:—

	Air dissolved in water.				Ordinary air.
Oxygen	..	34.43	..	..	21
Nitrogen	..	65.57	..	..	79
		<u>100.00</u>			<u>100</u>

(The composition is here expressed volumetrically.)

This superior solubility of oxygen is of vital importance to fish and other aquatic organisms, as it provides them with the oxygen necessary for respiration.

**Other Constituents of the Atmosphere.**—Although oxygen and nitrogen are the chief constituents of the atmosphere, small traces of other substances exist in it in varying quantities. Of these, carbon dioxide

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<sup>1</sup> That is, made to combine with oxygen.

exists in a proportion of about 4 volumes in 10,000 volumes of air, and, as we shall see hereafter, this substance is necessary for vegetable respiration. Air in which 1 per cent. of oxygen is replaced by carbon dioxide is unfit for animal respiration, and when the proportion reaches 10 per cent. it produces insensibility.<sup>1</sup> Hence the necessity for free ventilation, since in a crowded and confined room the amount of carbon dioxide is increased by the respiration of the persons present.

Water vapour is always present in the air in varying quantities; the amount of vapour contained in a given volume of air varying with the temperature, &c. At 25° C., for instance, one cubic metre of air contains 22½ grammes of water vapour, while at 0° C. this volume of air contains only 5.4 grammes. The formation of rain is thus easily understood when we remember that currents of air saturated with moisture at a certain temperature are frequently cooled down, and thus made to precipitate<sup>2</sup> a certain portion of their moisture as rain.

Ammonia, a pungent gas composed of nitrogen and hydrogen, also exists in minute quantities in the atmosphere; one million parts of air containing an average of about one part of ammonia. Other substances existing in the air are ozone and organic impurities.

### 3. NITROGEN.<sup>1</sup>

Symbol, N. Atomic weight, 14.

**Occurrence.**—This element occurs in the free state in the atmosphere, of which it constitutes  $\frac{1}{5}$  by bulk, and

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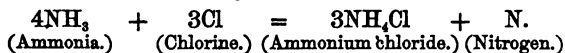
<sup>1</sup> Huxley, "Elementary Lessons in Physiology," p. 115.

<sup>2</sup> *L. præcipito*, to cast down. For further particulars on rain, snow, hail, fog, dew, mist, &c., the student may consult the volume on Physical Geography in this series of manuals.

<sup>3</sup> From the Greek *nitron*, nitre, and *gennaō*, I generate. Applied to this element because it enters into the composition of nitre (potassium nitrate).

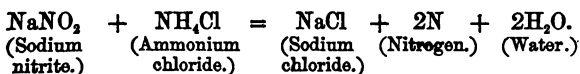
in most animal and vegetable substances in combination with other elements. Nitrogen occurs also in combination with oxygen and sodium as *Chili saltpetre*, and in combination with potassium and oxygen as ordinary *saltpetre*, or *nitre*, in India and other tropical countries.

**Preparation.**—We have already described methods by which this element can be prepared from atmospheric air. Two other processes which are sometimes used may be now considered. *Ammonia* has been already described as a compound consisting of nitrogen and hydrogen—it is, in fact, *nitrogen trihydride* ( $\text{NH}_3$ ). When ammonia is acted on by the element chlorine, the hydrogen is withdrawn to form *hydrogen chloride*, and the nitrogen is set free. The hydrogen chloride produced combines with other portions of the ammonia to form another compound, *ammonium chloride*, which will be considered subsequently. The changes undergone are expressed in symbols thus:—



The experiment is practically conducted by causing a stream of chlorine to bubble through a solution of ammonia in water. Each bubble causes a flash of light as it enters the ammonia solution, and the nitrogen is given off with effervescence, and may be collected in the usual way over the pneumatic trough.

Another mode of preparing nitrogen consists in heating *sodium nitrite* ( $\text{NaNO}_2$ ) with *ammonium chloride*, thus:—



**Properties.**—Nitrogen is a gas at all known temperatures and pressures, colourless, transparent, and inodorous. It is not combustible, nor does it support the

combustion of ordinary combustible bodies that burn in air or oxygen. Nitrogen is a most inactive element; it combines with hydrogen only when this gas is in the *nascent state*,<sup>1</sup> and with oxygen when a stream of electric sparks is passed through a mixture of these gases.

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*D.—COMPOUND OF NITROGEN WITH  
HYDROGEN.*

**4. AMMONIA.<sup>2</sup>**

Symbol,  $\text{NH}_3$ . Molecular weight, 17.

**Preparation.**—When organic substances containing nitrogen and hydrogen are heated in vessels from which the air is excluded, these two elements unite at the moment of their liberation to form ammonia. For the preparation of this substance clippings of horn and hides were formerly used—hence the term *hartshorn* sometimes applied to ammonia. The most abundant source of ammonia at present known is the liquor from the gas-works, in which ammonia exists produced by the distillation of coal, which contains both nitrogen and hydrogen. Ammonia combined with hydrogen chloride as ammonium chloride occurs native in certain volcanic regions, but it was formerly obtained from Egypt, where it was prepared by heating the excrement of camels; the name *sal-ammoniac* by which ammonium chloride is generally known being of Arabian origin.

Ammonia in the free state is usually prepared by heating this *sal-ammoniac* with calcium oxide (quick-lime). The apparatus employed for this purpose is shown on the next page.

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<sup>1</sup> A gas is said to be in the nascent state at the moment of its liberation. (*L. nascor*, to be born.)

<sup>2</sup> So called because one of its compounds was first prepared by the Arabs near the temple of Jupiter Ammon.

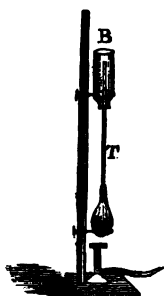
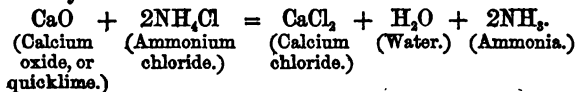


Fig. 13.—Preparation of ammonia gas.

A mixture of sal-ammoniac with about twice its weight of powdered quicklime is introduced into the dry glass flask *F*, and a layer of quicklime of about equal thickness is placed on the top of this mixture. The flask is fitted with a perforated cork, through which passes a straight glass tube (*T*). A gentle heat is now applied to the bottom of the flask, when the ammonia gas is liberated, and is dried by passing through the layer of quicklime, a substance which absorbs moisture greedily. Ammonia being a gas lighter than the air may be collected by upward displacement by inverting the bottle *B* over the glass tube *T*.

The chemical changes occurring in this reaction are thus symbolised :—



**Properties.**—Ammonia is a gas at ordinary temperatures and pressures colourless and invisible. It possesses a most pungent<sup>1</sup> odour, and will not support either combustion or animal life.

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<sup>1</sup> *L. pungo*, to prick or sting.



By virtue of its contained hydrogen ammonia gas is feebly combustible. When issuing into the air in a thin stream it takes fire on applying a lighted taper, and burns with a pale flame; mixed with oxygen the combustion becomes more energetic, and a stream of these two gases issuing from a tube will burn with a greenish flame on applying a lighted taper.

We have already had occasion to mention that ammonia is lighter than the air; its weight compared with an equal bulk of air is 0.59. Ammonia is extremely soluble in water; at ordinary temperatures and pressures water absorbs about 681 times its volume of the gas, which cannot therefore be collected over water at the pneumatic trough, but must be either collected over mercury or by upward displacement.

The aqueous<sup>1</sup> solution of ammonia gas causes red vegetable colours to become blue, and behaves in all respects like those substances termed *alkalies*, which we shall treat of subsequently. When submitted to great pressure or to a very low degree of cold (about 50° below 0°), ammonia gas passes into the liquid state: it is then a colourless liquid, which by a further application of cold and pressure becomes a white crystalline<sup>2</sup> solid.

Ammonia is, as we have already seen, decomposed by chlorine with liberation of its nitrogen. When the metals potassium and sodium, already employed to decompose water, are heated in a current of dry ammonia gas the nitrogen combines with the metal used, and the hydrogen is liberated. Decomposition, with the liberation of *both* constituents, occurs when ammonia is

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<sup>1</sup> Meaning, the solution in water. (L. *aqua*, water.) This solution is known by the trivial name of *spirits of hartshorn*, for reasons already described.

<sup>2</sup> A solid exhibiting a regular geometrical form is said to be crystalline. (G. *krystallös*, ice.)

submitted to a very high temperature, as by passing a spark-current for some time through a portion of the gas confined in a tube.

### 1. OXIDES AND ACIDS OF NITROGEN.

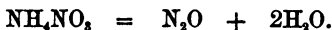
Nitrogen forms a series of five compounds with oxygen and three compounds with oxygen and hydrogen, termed *acids*. The oxides of nitrogen have already been utilised to illustrate the law of combination in multiple proportion (see p. 9). The student may now make himself acquainted with the names, methods of preparation, and properties of the members of this interesting series of compounds.

- (1) Nitrogen monoxide .....  $N_2O$ .
- (2) Nitrogen dioxide .....  $N_2O_2$ .
- (3) Nitrogen trioxide .....  $N_2O_3$ .
- (4) Nitrogen tetroxide .....  $N_2O_4$ .
- (5) Nitrogen pentoxide .....  $N_2O_5$ .

### 5. NITROGEN MONOXIDE.

Symbol,  $N_2O$ . Molecular weight, 44.

**Preparation.**—This compound is prepared by heating crystals of *ammonium nitrate* in a flask similar to that figured for preparing oxygen (p. 39). The gas may be collected over *warm* water at the pneumatic trough, as it is rather soluble in cold water. The ammonium nitrate splits up, when heated, into water and nitrogen monoxide, thus:—



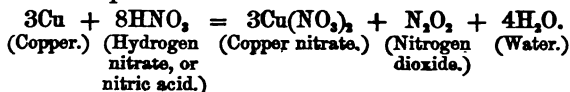
**Properties.**—At all ordinary temperatures this compound is a colourless and transparent gas, possessing a faint odour and a sweetish taste. It is not combustible, and is a good supporter of combustion. At ordinary temperatures 100 volumes of water dissolve 78 volumes of this gas. Nitrogen monoxide produces a peculiar intoxic-

cating effect when inhaled, and is for this reason sometimes termed *laughing gas*. When submitted to intense cold and pressure this gas can be obtained in the liquid and even in the solid state. When sodium or potassium is heated in the gas the oxygen combines with the metal, and the nitrogen is set free: a similar change occurs when a mixture of nitrogen monoxide and hydrogen is exploded by the application of a lighted taper—water being formed instead of the metallic oxide. This gas is sometimes called *nitrous oxide*.

## 6. NITROGEN DIOXIDE.

Symbol,  $N_2O_2$ . Molecular weight, 60.

**Preparation.**—By acting on metallic copper with nitric acid in a flask similar to that used for preparing hydrogen (p. 35). The reaction that takes place may be thus represented:—



**Properties.**—A colourless gas supporting combustion only with difficulty; has never been liquefied; forms a reddish-brown vapour in contact with free oxygen, owing to the formation of higher oxides. Called also *nitric oxide*.

## 7. NITROGEN TRIOXIDE.

Symbol,  $N_2O_3$ . Molecular weight, 76.

**Preparation.**—By cooling a mixture of four volumes of the foregoing oxide ( $N_2O_2$ ) with one volume of oxygen by means of a freezing mixture. Reaction:—



Also by warming a mixture of nitric acid with arsenic trioxide ( $As_2O_3$ ) or with starch.

**Properties.**—At ordinary temperatures an orange-red gas, condensing at  $-18^{\circ}\text{C}$ . to a blue liquid which emits red fumes in the air. Known also by the name of *nitrous anhydride*. It is soluble in ice-cold water, forming a blue solution which contains *nitrous acid* in solution, and this decomposes at higher temperatures into nitric acid and nitrogen dioxide.

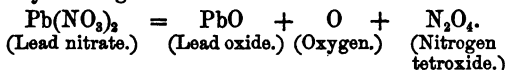
## 8. NITROGEN TETROXIDE.

Symbol,  $\text{N}_2\text{O}_4$ . Molecular weight, 92.

**Preparation.**—By submitting a mixture of two volumes of nitrogen dioxide and one volume of oxygen to a freezing mixture: Both gases must be thoroughly dried. Reaction:—



**Also by heating dried lead nitrate in a retort.**



**Properties.**—At ordinary temperatures a brown-red gas of a pungent and suffocating odour and acid taste. At a temperature of 9° below zero this compound forms colourless crystals; above this temperature it forms a greenish-yellow liquid which becomes redder as its temperature rises. It is sometimes termed *nitric peroxide*.

## 9. NITROGEN PENTOXIDE.

Symbol,  $\text{N}_2\text{O}_5$ . Molecular weight, 108.

**Preparation.**—By acting on silver nitrate heated to a temperature of about 63° C. with dry chlorine.



The silver nitrate is placed in a U-tube, heated in a vessel of hot water.

**Properties.**—Colourless transparent crystals melting at  $30^{\circ}$  and boiling at about  $45^{\circ}$ . It is called also *nitric anhydride*.

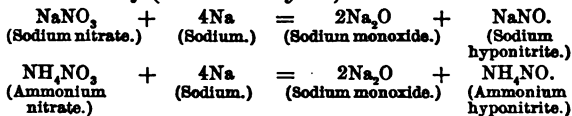
## 2. ACIDS OF NITROGEN.

- (1) Hyponitrous acid .....  $\text{HNO}$ .  
 (2) Nitrous acid .....  $\text{HNO}_2$ .  
 (3) Nitric acid .....  $\text{HNO}_3$ .

## 10. HYPONITROUS ACID.

Symbol,  $\text{HNO}$ . Molecular weight, 31.

**Preparation.**—By acting on sodium nitrate ( $\text{NaNO}_3$ ) or ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) with sodium alloyed with mercury (*sodium amalgam*<sup>1</sup>):—

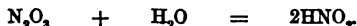


The mercury takes no active part in the reaction. The acid itself is unknown in the free state.

## 11. NITROUS ACID.

Symbol,  $\text{HNO}_2$ . Molecular weight, 47.

**Preparation.**—By dissolving nitrogen trioxide in water cooled down to near its freezing point, a blue solution containing this acid is formed in accordance with the reaction:—



On heating this solution it undergoes decomposition into nitric acid, nitrogen dioxide, and water, thus:—



Owing to this readiness of decomposition the free acid is but little known, but its compounds with metals, called *nitrites*, are much more stable, and can be better

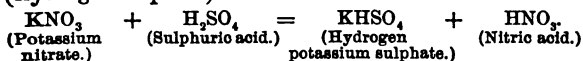
<sup>1</sup> A compound of quicksilver with another metal is called an *amalgam*. (*G. ama*, together; *gamōs*, a marriage.)

studied. Thus, when potassium or sodium takes the place of hydrogen in nitrous acid we have formed potassium nitrite ( $\text{KNO}_2$ ), or sodium nitrite ( $\text{NaNO}_2$ ).

## 12. NITRIC ACID.

Symbol,  $\text{HNO}_3$ . Molecular weight, 63.

**Preparation.**—This acid is the most important of the nitrogen acids, and is made in large quantities for manufacturing purposes. It is prepared by distilling potassium or sodium nitrate with sulphuric acid (hydrogen sulphate):—



For preparation on a small scale a glass retort may be used, but for manufacturing purposes cast-iron cylinders and stoneware condensing bottles are employed.

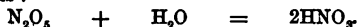
**Properties.**—Nitric acid is a transparent and highly corrosive<sup>1</sup> liquid, staining the skin a yellow colour. When pure it is colourless; but the acid of commerce is usually of a yellow colour, from the presence of other oxides of nitrogen in solution. The commercial acid has a specific gravity of about 1.52, and fumes in moist air. On distilling nitric acid a portion is at length obtained which boils under ordinary atmospheric pressure at  $120.5^\circ \text{C}$ . This acid of fixed boiling point has a specific gravity of 1.414, and contains 68 per cent. of  $\text{HNO}_3$ , the remainder being water. The point at which the aqueous acid boils, and the percentage of  $\text{HNO}_3$ , vary with the pressure. The greater part of the oxygen contained in nitric acid is readily imparted to other substances, so that this acid is said to be a powerful *oxidiser*. Like all acids, it turns vegetable blue colours to red. In combination with metals it forms a series of *salts*, called *nitrates*. Potassium

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<sup>1</sup> *L. corrodo*, to gnaw.

nitrate (called also nitre or saltpetre) is, as we have seen, sometimes used for the manufacture of the acid.

Nitric acid is formed in minute quantities by the direct union of nitrogen and oxygen, when a stream of electric sparks is passed through a mixture of these two gases in presence of moisture. It is also produced when nitrogen pentoxide is brought in contact with water, thus :—



**Summary.**—1. The atmosphere is a mixture of nitrogen with oxygen in the proportion of four volumes of the former to one volume of the latter gas.

2. Other constituents of the atmosphere are carbon dioxide, water vapour, ammonia, ozone, and organic impurities.

3. Nitrogen is generally prepared by removing the oxygen from air, either by means of burning phosphorus or red-hot copper.

4. One atom of nitrogen combined with three atoms of hydrogen forms ammonia. This substance is prepared by heating ammonium chloride with quicklime.

5. Nitrogen forms five oxides with oxygen and three acids with oxygen and hydrogen.

6. Of the acids of nitrogen, the most important is nitric acid, obtained by distilling potassium or sodium nitrate with sulphuric acid.

7. The hydrogen in nitric acid, when replaced by metals, gives rise to a series of salts called *nitrates*.

8. Under similar circumstances, nitrous acid gives rise to a series of salts termed *nitrites*.

## CHAPTER IV.

### ON THE ATOMIC COMPOSITION OF MOLECULES.

#### A.—VOLUMETRIC COMBINATION.<sup>1</sup>

**Introduction.**—We have hitherto concerned ourselves solely with the laws of combination *by weight*. We have seen that matter is built up of inconceivably small par-

<sup>1</sup> That is, combination by volume.

ticles called *molecules*, and that molecules are in their turn composed of *atoms*. The molecule has been defined as the smallest portion of an element that can exist in the free state, while the atom has been defined as the smallest portion by weight of an element that can exist in combination; the unit of hydrogen being made the standard of comparison. We have seen that the elements, in entering into combination with one another, always combine in certain fixed proportions by weight; these numbers, referred to hydrogen as unity, being termed in consequence the *combining weights*. Chemical combination being supposed to take place by the juxtaposition of the atoms of dissimilar elements, these combining weights are regarded also as the weights of the elementary atoms, and are consequently called also *atomic weights*. We have likewise seen that in most cases the elementary molecule consists of two atoms: in a few cases it consists of one atom, in one case (ozone) of three atoms, and in other cases of four atoms. It will be now advantageous to make ourselves acquainted with the method by which the atomic composition of molecules is ascertained; and we shall best approach this subject through the laws of volumetric combination.

**Atomic Volumes.**—The volumes occupied by the atomic weights of those elements that are gaseous at ordinary temperatures, or can be made into vapour by heat, are known as the *atomic volumes*. The atomic volume may be thus defined as *the volume occupied by a weight of the element proportional to its atomic weight*.

It is found by experiment that the atomic volumes of the elementary gases are equal—in other words, one part by weight of hydrogen, 16 of oxygen, 14 of nitrogen, and 35.5 of chlorine all occupy the same volume when measured under similar conditions of temperature and pressure. The atomic weights and specific gravities (referred to hydrogen) of these



elements are therefore identical, and a new meaning is thus attached to certain of our symbolic expressions; for the symbols O, N, Cl, &c., in addition to 16, 14, and  $35\frac{1}{2}$  parts by weight of oxygen, nitrogen, and chlorine respectively, now stand for *one volume* of each of these elements, and moreover represent to us that these volumes are respectively 16, 14, and  $35\frac{1}{2}$  times heavier than an equal volume of hydrogen. The symbols formerly used to represent combining or atomic *weights* now express also combining or atomic *volumes*, and equations representing the *weights* of the elements concerned in a reaction now also represent the *volumes* of the elements so concerned.

With the knowledge thus acquired it now becomes possible to give another definition of the term "atomic weight." This may be defined as "The weight of the element which, in the form of gas or vapour, occupies, under like conditions of temperature and pressure, the same volume as one part by weight of hydrogen. (*Frankland*).

The atomic volumes of the elementary bodies are not all equal to *one*. The elements mercury, cadmium, and zinc have atomic volumes equal to *two*, while phosphorus and arsenic have atomic volumes equal to *one-half* that of hydrogen; that is, the volume occupied by 200, 112, and 65 parts by weight of mercury, cadmium, and zinc respectively is double the volume occupied by one part by weight of hydrogen, while the volume occupied respectively by 31 and 75 parts of phosphorus and arsenic is only half the volume occupied by one part by weight of hydrogen. These anomalous<sup>1</sup> cases break the uniformity of the rule that the combining volumes of the elementary gases are equal, but as facts they cannot be ignored, although we are as yet in perfect ignorance as to the reason of their existence.

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<sup>1</sup> Departing from established rules. (G. α, not; νόμος, a law.)

**Molecular Volumes.**—The volume occupied by the molecular weight of an element or compound is its *molecular volume*. This subject will be best approached by studying the volumes occupied by the molecules of *compound* gases and vapours.

It might be imagined that the volume occupied by a compound molecule consisting of many atoms would be the sum of the atomic volumes of its constituents. That this is not the case may be seen from the results given below :—

Vols.	Vols.	Vols.
1 of hydrogen	+ 1 of chlorine	= 2 of hydrogen chloride.
1 of nitrogen	+ 3 of hydrogen	= 2 of ammonia gas.
2 of nitrogen	+ 1 of oxygen	= 2 of nitrogen monoxide.
2 of nitrogen	+ 3 of oxygen	= 2 of nitrogen trioxide.
2 of hydrogen	+ 1 of oxygen	= 2 of water gas.

It thus appears that the molecular volumes of these compound gases are all equal, and the rule is found to hold good in nearly all cases. Where the sum of the atomic volumes exceeds two, condensation must of course take place. In the case of hydrogen chloride, for example, two volumes exist before combination and two volumes after, so that no condensation takes place. In the case of water, 3 volumes are condensed to 2, so that a contraction of  $\frac{1}{3}$  of the volume of the mixture takes place, as we have already had occasion to mention in connection with the subject of the eudiometrical analysis of the air (p. 47). With ammonia 3 volumes of hydrogen and 1 volume of nitrogen contract to 2 volumes, so that the mixture (supposing direct combination possible) would contract to half its original volume.

No matter how many atoms compose the molecule, the *product volume*—except in some few cases, to be considered hereafter—is always the same; that is, it occupies the same volume as two parts by weight of hydrogen. From this follows the law that *equal volumes of compound gases and vapours contain the same number*

*of molecules.* The law thus arrived at from chemical considerations is enforced by other considerations of a physical nature; but into these we cannot here enter. That this law holds good also for *elementary* gases and vapours is proved by similar considerations.

Assuming the molecular weight of hydrogen to be twice its atomic weight, the molecular volume of nearly all compound gases is thus made equal to the molecular volume of hydrogen. A comparison of the volume weights of the elements oxygen, chlorine, bromine, iodine, fluorine, nitrogen, sulphur, and selenium with the volume weight of hydrogen (two parts by weight or two volumes representing one molecule) shows that these gases contain two atomic weights to the molecule—the molecular weight of oxygen, for instance, being 32; and of nitrogen, 28. The assumption that the molecular weight of hydrogen is double its atomic weight, or, in other words, that its molecule contains two atoms, is warranted by the following reasoning:—Conceive two equal volumes of hydrogen and chlorine to be mixed and made to combine so as to form hydrogen chloride. We know from experiment that no contraction of volume occurs. Now let us imagine that the volume of hydrogen chloride contains 100 molecules: it follows from this that both volumes of hydrogen and chlorine used contain each 50 molecules; because equal volumes of elementary and compound gases contain the same number of molecules. The state of affairs now reached may be thus represented:—

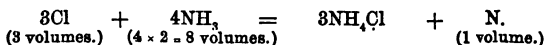
H 50 molecules.
Cl 50 molecules.

HCl 100 molecules.
HCl

Now, it will be seen from this diagram that the 100 molecules of hydrogen chloride contain 100 *atoms* of hydrogen and 100 *atoms* of chlorine; but the volume of hydrogen taken contained 50 molecules; consequently, 50 molecules of hydrogen have been distributed among 100 atoms of chlorine, and each hydrogen molecule has, therefore, divided into *two* parts or atoms.

The method by which the atomic composition of a molecule is ascertained will now become evident. It is only necessary to weigh a volume of the element equal to two volumes of hydrogen, and the number of atomic weights contained in this number gives the number of atoms contained in the molecule. Since the atomic volumes of mercury, cadmium, and zinc are *double* the atomic volume of hydrogen, it follows that the atomic and molecular weights of these elements are identical, and that their molecule contains but one atom. With phosphorus and arsenic, on the other hand, the volume occupied by the atom is only half the volume occupied by the atom of hydrogen; so that into the volume occupied by two atoms of hydrogen (one molecule) we could get four atomic volumes (atoms) of these elements, and their molecules are therefore *tetratomic*, and their molecular weights in consequence four times their atomic weights. These remarks may be applied by the student to all the cases given in the table on p. 13.

**Volume Reactions.**—It will be here interesting to study from this volumetric standpoint some reaction with which we have already made ourselves acquainted. We will select for this purpose the decomposition of ammonia by chlorine. We know, from what has just been said, that the formula of a compound generally stands for two volumes, so that the reaction may be thus expressed:—



From this we learn, theoretically, that three volumes

of chlorine liberate one volume of nitrogen; and we can prove this experimentally, as follows:—

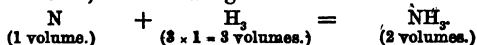


Fig. 14.

Decomposition of ammonia by chlorine.

A straight glass tube (Fig. 14) is filled with chlorine, and then divided by means of india-rubber rings into three equal portions. The open end of the tube is fitted with a perforated cork, through which passes the globe-funnel *f*, provided with a glass stopcock. This funnel is filled with a solution of strong ammonia, which, by turning the stopcock, is allowed to fall into the chlorine drop by drop. When the reaction is completed, nitrogen and ammonium chloride are the only products: the latter dissolves easily in water. The tube must be opened carefully under water, when the liquid will rise and fill it to the extent of two of the divisions, leaving the other division full of a gas, which will on examination be found to consist of nitrogen. We thereby prove that the three volumes of chlorine have liberated one volume of nitrogen.<sup>1</sup>

Similarly with regard to the constitution of ammonia gas itself. Could we produce this substance directly from its elements, the following would be the reaction:<sup>2</sup>—



Conversely, if ammonia could be split up into its constituent elements, these, when liberated, would occupy double the volume of the ammonia used, because four volumes have become condensed to two. This admits of experimental demonstration.

<sup>1</sup> We owe this experiment to Dr. Hofmann (Introd. to Modern Chemistry, p. 54 *et seq.*).

<sup>2</sup> It has been recently found that under the influence of induced electricity nitrogen and hydrogen combine directly to form ammonia.



Fig. 15.  
Apparatus for the  
decomposition of  
ammonia gas.

A tube of the form shown in Fig. 15, after being filled with mercury, has a certain quantity of ammonia gas passed up into its sealed limb. The mercury is brought to the same level in both limbs by allowing the excess to run off through the little stopcock shown at the bottom of the right limb. This adjustment of level is necessary to relieve the contained gas from

excess of pressure, which would otherwise cause it to contract, and we should not get a fair measurement. The height of the ammonia gas being marked by an india-rubber ring, a stream of electric sparks from an induction coil is allowed to traverse the gas for some time by means of two platinum wires sealed into the tube near its closed end; these wires nearly meeting inside the tube. After the decomposition is effected and the level of the mercury again restored, it will be found that the gas has doubled its volume, thereby proving that in ammonia 3 volumes of hydrogen and 1 volume of nitrogen are condensed to 2 volumes.

Another good example is furnished by nitrogen monoxide ( $N_2O$ ), a gas which we have already studied. An inspection of the formula of this gas shows us that it contains its own volume of nitrogen; and we prove this to be the case by the following experiment:—



Fig. 16.  
Tube for the decomposition  
of nitrogen monoxide.

A tube of hard glass sealed at one end is bent into the form shown in Fig. 16. The tube is filled with mercury, and then about half filled with nitrogen monoxide. A fragment of potassium is now passed up into the gas, and shaken into the bend of the

tube so as to lodge at the point P. The open end of the tube is firmly closed by the thumb (under mercury), and heat applied to the bend of the tube so as to ignite the potassium, which combines with the oxygen, forming an oxide of potassium, while the nitrogen is liberated. After the combustion of the potassium the thumb is removed, and when the tube is cool the nitrogen will be found to occupy precisely the same volume as the nitrogen monoxide originally used, thereby proving that this gas contains its own volume of nitrogen.

Finally, with regard to water, it can be shown that the 3 volumes of gas, when mixed (2 volumes of hydrogen and 1 volume of oxygen), become 2 volumes when combined chemically. This is effected by exploding the gases in a tube kept at a temperature above the boiling point of water, so that the water formed by the combination remains in the state of vapour.

**Dissociation.**—The law that the molecular volume of compound gases is equal to the molecular volume of hydrogen meets with notable exceptions in the case of certain compounds, such as nitrogen dioxide ( $N_2O_2$ ), nitrogen tetroxide ( $N_2O_4$ ), phosphorus pentachloride ( $PCl_5$ ), ammonium chloride ( $NH_4Cl$ ), and some others. In these cases the molecular volume is *double* the molecular volume of hydrogen. With many of these compounds, however, heat is necessary to bring the compound into the state of vapour; and there is reason to believe that under the influence of heat these compounds undergo decomposition into two compounds, each occupying the regular molecular volume. This form of decomposition has been termed *dissociation*. Thus, phosphorus pentachloride is supposed to split up into phosphorus trichloride and free chlorine:—



### B.—CORRECTIONS FOR TEMPERATURE AND PRESSURE.

**Law of Charles.**<sup>1</sup>—When heat is applied to a gas it expands, when cooled it contracts.<sup>2</sup> It is obvious, therefore, that in the comparison of gaseous volumes we must either operate under like conditions of temperature or else find some method of reducing a volume of gas, measured at any given temperature, to any other temperature by calculation. As it is impossible to command the same temperature at all times, the latter method is resorted to; and the student may here advantageously apply himself to the study of this method, although it belongs in reality to the domain of physics.

That fraction of itself by which a volume of gas increases when heated through one degree is termed its *coefficient of expansion*. The coefficient of expansion for all gases is very nearly the same, being  $\frac{1}{273}$  or .003665. This law was first discovered by Charles, and was subsequently investigated by Dalton, Gay-Lussac, Rudberg, Dulong and Petit, Magnus and Regnault, &c. Although for all purposes of calculation the coefficient of expansion may be considered the same for all gases, this is not strictly the case, since certain gases depart to a very small extent from the rule.

The knowledge of this coefficient of expansion enables us to reduce any gaseous volume of a known temperature to the volume occupied at some standard temperature; the freezing point of water (0° C.) being by universal consent selected for this purpose. The

---

<sup>1</sup> This law is frequently referred to as that of Gay-Lussac or Dalton.

<sup>2</sup> A familiar illustration of this fact may be obtained by partially filling a bladder with air and tying up the mouth. On warming the bladder before a fire the enclosed air expands and the bladder becomes tightly stretched.



data for such a calculation are supplied when this coefficient is known, for—

1	volume of gas at 0° C. becomes	$1 + \cdot 003665$	at 1° C.
1	"	$1 + (\cdot 003665 \times 2)$	" 2° C.
1	"	$1 + (\cdot 003665 \times 3)$	" 3° C.
1	"	$1 + (\cdot 003665 \times t)$	" $t^\circ$ C.

Suppose, for example, that a certain volume of gas measures 150 cubic centimetres at 10° C., and we require to know what volume it will occupy when reduced to the standard temperature.

We know for a fact that  $1 + (\cdot 003665 \times 10) = 1\cdot 03665$  volumes at 10° C. become 1 volume at 0° C.; so that—

$$1\cdot 03665 : 1 = 150 : x.$$

Whence  $x = 144\cdot 6$  cub. cent.

Again, 150 volumes are measured at 0° C.: what will they become when heated to 15° C.?

Here 1 volume at 0° C. becomes  $1 + (\cdot 003665 \times 15) = 1\cdot 054975$  at 15° C.; so that—

$$1 : 1\cdot 054975 = 150 : x = 158\cdot 2.$$

As a final example—what will 150 measures of gas at 15° C. become when reduced to — 10° C. (10° below 0° C.)?

Here,  $1 + (\cdot 003665 \times 15) = 1\cdot 054975$  volumes at 15° C. become  $1 - (\cdot 003665 \times 10) = \cdot 96335$  at — 10° C.; so that—

$$1\cdot 054975 : \cdot 96335 = 150 : x = 136\cdot 9.$$

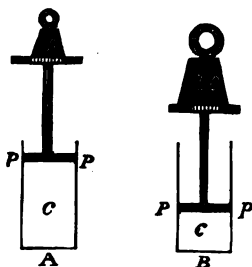


Fig. 17.  
Illustration of Boyle and  
Mariotte's law.

**Law of Boyle and Mariotte.**—When a gas is submitted to pressure it contracts; when the pressure is removed it resumes its original volume. It is obvious, therefore, that in comparing gaseous volumes account must be taken of the pressure under which the gas is measured, and a correction applied. The pressure

is measured by the *barometer* already described on p. 44.

Imagine a cylinder (Fig. 17, c) into which the piston *pp* slides "air-tight" and without friction. This cylinder is connected with a tray for carrying weights by means of an upright rigid rod. A weight, say, of 10 kilogrammes being placed on the tray, the piston sinks in the cylinder, and reaches a certain level, shown in *A*. This level being marked, a 20-kilogramme weight is substituted for the weight formerly used, when the piston will be found to sink in the cylinder to such an extent that the enclosed volume of air is only half its former volume (see *B* of the above figure). By *doubling* the pressure we therefore *halve* the volume—hence the law known from its discoverers as Boyle and Mariotte's law:—

*The volume occupied by a gas varies inversely as the pressure to which it is subjected.*

This law, like the foregoing law of Charles, is not absolutely true under all conditions. Under very high pressures, for instance, all gases depart from the rule to a certain extent, and near their liquefying points also the volumes diminish somewhat more rapidly than in the ratios required by the law as above set forth. The deviations are, however, so small that the absolute truth of the law may be assumed for our present purpose.

A knowledge of this law enables us to reduce a volume of gas, measured at any known pressure, to a volume that would be occupied at some standard pressure; the weight of a barometrical column of mercury 760 millimetres high being fixed upon for this purpose.

Suppose, for instance, we have 100 volumes of air under a pressure of 758 millim., and we require to know what volume this will occupy under the standard pressure. Then, since the volume varies inversely as the pressure—

$$760 : 758 = 100 : x = 99.7$$

Again, 100 volumes of gas are measured at 765 millim.: what will they become at 758 millim.?

$$758 : 765 = 100 : x = 100.9.$$

**General Formula.**—It generally happens that *both* of the above corrections have to be applied to the volume measured in experimental determinations, so that it facilitates calculation to apply both corrections at once by means of a formula which we may now build up. The standard temperature and pressure, it must be remembered, are  $0^{\circ}\text{C.}$  and 760 millim. barometrical column. Suppose, now, the following question be presented for solution:—

A volume of gas measures 150 cubic centim. at  $10^{\circ}\text{C.}$  and 758 millim. pressure: what volume will this become at the standard temperature and pressure?

Let us first apply each correction separately.

For temperature:—

$$1 + (.003665 \times 10) : 1 = 150 : x = 144.7$$

For pressure:—

$$760 : 758 = 144.7 : x = 144.3$$

In practice it would be more convenient to work both these proportions together, thus, calling the required number  $x$ :—

$$x = \frac{150 \times 1 \times 758}{[1 + (.003665 \times 10)] \times 760} = 144.3$$

Substituting abstract for concrete symbols, we may now build up a formula applicable to all cases.

The volume at standard temperature and pressure may be called  $V_0$ , the volume at time of measuring  $V$ .

The pressure at the time of measuring may be represented by  $p$ , and the temperature at this same time by  $t$ . Then:—

$$V_0 = \frac{Vp}{(1 + .003665t) \times 760}$$

The student will do well to commit this formula to memory so as to have it ready for use in any calculation.

**The Crith and its uses.**—Since the molecules of all gases occupy the same volume in the gaseous state, the

specific gravity of any gas, simple or compound, referred to hydrogen as unity, may be readily found by dividing the weight of the molecule by 2.

For instance, the molecule of oxygen weighs 32—that is, a given volume of oxygen is 32 times heavier than two volumes of hydrogen, or one volume is  $\frac{32}{2}=16$  times heavier than an equal volume of hydrogen; in other words, its specific gravity is 16. Two volumes of mercury vapour weigh 200 times as much as an equal volume of hydrogen, hence its specific gravity is  $\frac{200}{2}=100$ ; and, finally, the molecule of phosphorus in the gaseous state weighs 124 times as much as the molecule of hydrogen, and its density is consequently  $\frac{124}{2}=62$ .

The same rule obviously applies to compounds. The molecular weight of a compound having been defined as the sum of the atomic weights of its constituents, it is only necessary, in order to obtain the density of a compound, to add up the atomic weights of the constituents, and divide this number by 2. The formula for ammonia being  $\text{NH}_3$ , its molecular weight is  $14+3=17$ ; but as this weight occupies twice the volume of one part by weight of hydrogen, its density is  $\frac{17}{2}=8.5$ . With compounds which undergo dissociation, however, it is clear that we must make the divisor 4 instead of 2, since the molecule of such a compound occupies, in the gaseous state, four times the volume of one part by weight of hydrogen. Thus the vapour densities of nitrogen dioxide and nitrogen tetroxide are respectively—

$$\frac{(14 \times 2) + (16 \times 2)}{4} = 15, \text{ and } \frac{(14 \times 2) + (16 \times 4)}{4} = 23.$$

For practical purposes it is often necessary to calculate the *absolute weight* of a given volume of gas. As we have learnt how to calculate the density of any gas referred to hydrogen, it is clear that we could easily calculate the absolute weight of a gas if we fixed upon the weight of a given volume of hydrogen and made this a standard multiplier. The volume selected for

this purpose by Dr. Hofmann is one *cubic decimetre* or *litre*; and this weight of hydrogen—termed, for brevity, the *crith*<sup>1</sup>—is at the standard temperature and pressure ·0896 grammes.

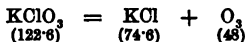
By means of this crith, the absolute weight of any gas, simple or compound, can be easily calculated. The density of oxygen, for instance, being 16, one litre of this gas weighs 16 criths =  $16 \times \cdot 0896 = 1\cdot4336$  grammes. Similarly, one litre of ammonia weighs 8·5 criths =  $8\cdot5 \times \cdot 0896 = 0\cdot7616$  grammes, and one litre of nitrogen tetroxide 23 criths =  $23 \times 2\cdot0896 = 2\cdot0608$  grammes.

### C.—CHEMICAL CALCULATIONS.

We may now proceed to discuss some problems, the solution of which depends upon the application of principles laid down in the foregoing portions of the chapter. Problems involving arithmetical calculations are frequently presented for solution, so that the student is recommended to follow closely the methods employed in working out the answers to the following questions:—

(1) How much oxygen by weight can be obtained from 100 grammes of potassium chlorate; and how much potassium chloride is formed in the reaction?

First state the reaction in full:—



From this we see that 122·6 parts of KClO<sub>3</sub> yield 48 parts of oxygen. Therefore—

$$\begin{array}{l} 122\cdot6 : 100 :: 48 : x \\ x = 39\cdot15 \end{array}$$

Similarly, 122·6 parts of KClO<sub>3</sub> yield 74·6 parts of KCl. Therefore 100 parts yield—

$$\begin{array}{l} 122\cdot6 : 100 :: 74\cdot6 : x \\ x = 60\cdot84 \end{array}$$

---

<sup>1</sup> G. *krithe*, a barleycorn; figuratively, a small weight.

*Answer* :—39.15 grammes oxygen; 60.84 grammes potassium chloride.

(2) What is the percentage composition of a substance having the formula  $\text{NH}_4\text{Cl}$ ?

N .....	14.0
H <sub>4</sub> .....	4.0
Cl.....	35.5
	<hr/>
	53.5
	<hr/>

We see from the above that 53.5 parts of the substance contain 14 parts of N and 4 parts of H; so that 100 parts contain—

$$\begin{array}{l} 53.5 : 100 :: 14 : x = 26.16 \text{ parts nitrogen} \\ 53.5 : 100 :: 4 : x = 7.47 \text{ „ hydrogen} \end{array}$$

The chlorine may be found by difference :—

$100 - (26.16 + 7.47) = 66.37$ . Whence the percentage composition is—

N .....	26.16
H .....	7.47
Cl .....	66.37
	<hr/>
	100.00
	<hr/>

(3) Find the percentage composition by volume of ammonia gas.

N .....	1 vol.
H <sub>3</sub> .....	3 vols.
	<hr/>
	2 vols.
	<hr/>

2 volumes of  $\text{NH}_3$  contain 3 volumes of H; therefore 100 contain—

$$\begin{array}{l} 2 : 100 :: 3 : x = 150 \text{ volumes of hydrogen} \\ 2 : 100 :: 1 : x = 50 \text{ „ nitrogen} \\ \hline 100 \text{ „ ammonia} \end{array}$$

(4) What is the weight of 100 litres of oxygen measured at  $15^\circ \text{C}$ . and 745 mm. bar.?

Find first what volume 100 litres at  $15^\circ \text{C}$ . and 745 mm. bar. become at  $0^\circ$  and 760 mm. bar., by applying the formula given on p. 72:—

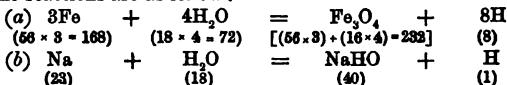
$$\frac{100 \times 745}{[1 + (.003665 \times 15)] \times 760} = 92.91$$

Next find the weight of 92.91 litres at  $0^\circ$  and 760 mm.

$$92.91 \times (16 \times .0896) = 133.19 \text{ grms.}$$

(5) How much hydrogen measured at  $19^\circ$  C. and 753 mm. bar. can be obtained from water—(a) by the action of 500 grms. of iron at a red heat; (b) by the action of 500 grms. of sodium? What would this last quantity of gas measure at  $-8^\circ$  C. and 764 mm. bar.?

The reactions are as follow:—



Here 168 grms. of Fe liberate 8 grms. of hydrogen; so that 500 grms. would liberate—

$$168 : 500 :: 8 : x = 23.8$$

We have thus found the *weight* of hydrogen obtained, and we have now to find what this weight of hydrogen would measure at  $19^\circ$  C. and 753 mm. bar.

.0896 grms. of H at  $0^\circ$  and 760 mm. occupy 1 litre; so that 23.8 grms. would occupy  $\frac{23.8}{.0896} = 265.6$  litres, and 265.6 litres at  $0^\circ$  C. and 760 mm. would become at  $19^\circ$  C. and 753 mm.—

For temperature:—

$$1 : 1 + (.003665 \times 19) :: 265.6 : x$$

For pressure:—

$$\begin{array}{l} 753 : 760 :: 265.6 : x \\ \text{Whence } x = \frac{265.6 \times [1 + (.003665 \times 19)] \times 760}{753} = 286.7 \end{array}$$

From equation (b) we see that 23 parts of sodium liberate 1 part of hydrogen; so that 500 grms. liberate—

$$23 : 500 :: 1 : x = 21.7$$

Then 21.7 grms. occupy, at  $0^\circ$  and 760 mm.,  $\frac{21.7}{.0896} = 242.1$  litres; and 242.1 at  $0^\circ$  and 760 mm., become, at  $19^\circ$  and 753 mm.—

$$\frac{242.1 \times [1 + (.003665 \times 19)] \times 760}{753} = 261.3 \text{ litres.}$$

We have finally to find what 261.3 litres at  $19^\circ$  and 753 mm. would become at  $-8^\circ$  C. and 764 mm. bar.

For temperature:—

$$1 + (.003665 \times 19) : 1 - (.003665 \times 8) :: 261.3 : x$$

For pressure:—

$$\begin{array}{l} 764 : 753 :: 261.3 : x \\ \text{Therefore } x = \frac{[1 - (.003665 \times 8)] \times 261.3 \times 753}{764 \times [1 + (.003665 \times 19)]} = 233.7 \end{array}$$

(6) A substance is found by analysis to possess the following composition :—

Sodium .....	27.06
Nitrogen .....	16.47
Oxygen .....	56.47
	<hr/>
	100.00

What is its formula?

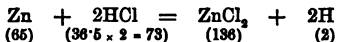
Divide each number by the atomic weight of its respective element, and the quotient evidently gives the number of atoms. Thus :—

Sodium .....	$\frac{27.06}{23} = 1.17$
Nitrogen .....	$\frac{16.47}{14} = 1.17$
Oxygen .....	$\frac{56.47}{16} = 3.52$

From this we should at first be inclined to deduce the formula  $\text{Na}_{1.17} \text{N}_{1.17} \text{O}_{3.52}$ ; but the atom is by definition an indivisible quantity, so that we substitute the more simple ratios of  $\text{NaNO}_3$ , the substance being *sodium nitrate*.

(7) How much zinc and hydrochloric acid are required to produce 100 litres of hydrogen when the temperature is  $16^\circ \text{C}$ . and the barometer stands at 754 mm.?

Reaction :—



Now the temperature being *higher* and the pressure *lower* than the standard, it is obvious that in 100 litres measured at  $16^\circ$  and 755 mm. there is *less* weight of gas than in 100 litres measured at the standard temperature and pressure. We have to find, therefore, the actual weight of hydrogen in 100 litres measured at  $16^\circ$  and 755 mm. bar.

Reduce by means of formula on p. 72 :—

$$\frac{100 \times 755}{760 \times [1 + (.003665 \times 16)]} = 93.8$$

The actual weight of 93.8 litres of  $\text{H}$  is  $93.8 \times .0896 = 8.40$  grms. Turning to the equation, we find that to produce 2 parts of hydrogen we must take 65 parts of zinc and 73 parts of hydrochloric acid: to produce 8.4 grms. of hydrogen we therefore require, of zinc—

$$2 : 8.4 :: 65 : x = 273 \text{ grms. ;}$$



and of hydrochloric acid—

$$2 : 8.4 :: 73 : x = 306.6 \text{ grms.}$$

(8) Find the weight in grammes of 10 litres of the following gases measured at  $0^\circ$  and 760 mm.: ammonia, nitrogen monoxide, nitrogen dioxide, atmospheric air (dry), oxygen, and nitrogen.

The relative densities of the gases referred to hydrogen must be first found :—

$$\begin{aligned} \text{Ammonia} &= \text{NH}_3 = \frac{14+3}{2} = 8.5. \quad \text{Nitrogen monoxide} = \text{N}_2\text{O} = \\ &= \frac{(14 \times 2) + 16}{2} = 22. \quad \text{Nitrogen dioxide} = \text{N}_2\text{O}_2 = (14 \times 2) + (16 \times 2) \\ &= 60. \quad \text{This weight, however, corresponds to 4 vols., so that the} \\ &\text{density is } \frac{60}{4} = 15. \quad \text{We may consider atmospheric air, for the} \\ &\text{purposes of the present calculation, to be composed, in 5 vols.,} \\ &\text{of 4 vols. of nitrogen and 1 vol. of oxygen, so that its density is} \\ &= \frac{(14 \times 4) + 16}{5} = 14.4. \quad \text{Oxygen} = 16. \quad \text{Nitrogen} = 14. \end{aligned}$$

Now 1 litre of H weighs .0896 grms., so that 10 litres weigh .896 grms., or 10 criths. The densities found above multiplied into this number give the actual weight of 10 litres :—

Ammonia .....	8.5	$\times .896$	$= 7.61$	grms.
Nitrogen monoxide...	22	$\times .896$	$= 19.71$	"
" dioxide.....	15	$\times .896$	$= 13.44$	"
Atmospheric air .....	14.4	$\times .896$	$= 12.90$	"
Oxygen.....	16	$\times .896$	$= 14.33$	"
Nitrogen .....	14	$\times .896$	$= 12.54$	"

(9) Equal volumes of oxygen, hydrogen, and water-gas are measured at the same temperature and pressure. The oxygen is found to weigh 40 grms. Required the weights of the other gases.

The specific gravity of oxygen (referred to hydrogen) being 16, a given volume of hydrogen weighs  $\frac{1}{16}$  of an equal vol. of oxygen. There are 40 grms. of oxygen, so that the hydrogen weighs  $\frac{1}{16} \times 40 = 2.5$  grms.

The specific gravity of water-gas (referred to hydrogen) is  $\frac{16+1}{1} = 9$ , so that a given vol. of this gas weighs 9 times as much as an equal volume of hydrogen. There are 2.5 grms. of this last gas: the water-gas consequently weighs  $2.5 \times 9 = 22.5$  grms.

**Diffusion of Gases.**—The air consists of gases of different densities, as we have already had occasion to

mention; nitrogen being 14 and oxygen 16 times heavier than hydrogen, bulk for bulk, while carbon dioxide is no less than 22 times heavier than an equal volume of hydrogen. How does it happen, then, that the air exhibits such constancy of composition from whatever source it is obtained? Why do not the different gases separate into layers according to their densities, the carbon dioxide sinking to the bottom, the oxygen resting on this, and the nitrogen on the oxygen? In reply to this question we shall first describe an experiment.



Fig. 18.  
Diffusion of oxygen  
and hydrogen.

Let two soda-water bottles be filled, one with oxygen, the other hydrogen, and after connecting them by a glass tube passing through corks fitted into the necks, let the bottles be supported in the position shown in the figure for some hours. Now we know that hydrogen by itself burns quietly, while oxygen does not burn at all, under ordinary circumstances. On disconnecting the bottles after the conclusion of the experiment, it will be found that the gas in each bottle explodes on the application of a lighted taper to the mouth, thereby proving that the gases have *mixed* in opposition to the law of gravity, some of the light hydrogen having passed downwards, and some of the heavy oxygen having passed upwards. If a plug of some porous substance—such as plaster of Paris—is placed in the glass tube, it does not in any way interfere with the final result. This property of intermixing is possessed by all gases and vapours, and is known as the power of *diffusion*. It is this power of diffusion that keeps the constituent gases of the atmosphere in a state of perfect mixture.

All gases do not diffuse into one another with the same velocity. The law of diffusion, first discovered by Graham, is thus expressed:—*The diffusive power of a gas varies inversely as the square root of its density.*

The diffusibility of a gas may be estimated by the following simple piece of apparatus.



Fig. 19.  
Graham's  
diffusion tube.

It consists of a glass tube about an inch in diameter at the top, and from six to fourteen inches long, open at the narrow end, and having the wide end plugged with a thin plate of some porous substance—such as plaster of Paris or black-lead.<sup>1</sup> The tube being partially or entirely filled with the gas to be experimented upon over the mercurial trough, an air-tight cap, which protects the porous plug, is removed, and the gas allowed to diffuse into the air, a certain quantity of which passes at the same time into the tube. The velocity of diffusion of various gases is shown in the following table:<sup>2</sup>—

Name of Gas.	Density. Air = 1.	Square root of Density.	$\frac{1}{\sqrt{\text{Density}}}$	Velocity of Diffu- sion. Air = 1.
Hydrogen (H).....	0.06926	0.2632	3.7794	3.8300
Marsh gas (CH <sub>4</sub> ).....	0.55900	0.7400	1.3375	1.3440
Carbon monoxide (CO) ...	0.96780	0.9837	1.0165	1.0149
Nitrogen (N) .....	0.97130	0.9856	1.0147	1.0143
Ethylene (C <sub>2</sub> H <sub>4</sub> ) .....	0.97800	0.9889	1.0112	1.0191
Oxygen (O).....	1.10560	1.0515	0.9510	0.9487
Hydrogen sulphide (H <sub>2</sub> S)	1.19120	1.0914	0.9162	0.9500
Nitrogen monoxide (N <sub>2</sub> O).	1.52700	1.2357	0.8092	0.8200
Carbon dioxide (CO <sub>2</sub> ).....	1.52901	1.2365	0.8087	0.8120
Sulphur dioxide (SO <sub>2</sub> ) ...	2.24700	1.4991	0.6671	0.6800

<sup>1</sup> Artificially compressed black-lead must be used, not the native graphite.

<sup>2</sup> This table is adapted from Watt's "Dictionary of Chemistry," vol. ii., p. 814.

The gases in the above table are arranged in the order of their densities, so that while the numbers in the first and second columns are increasing, the numbers in the last column, expressing the velocity of diffusion, are diminishing, because the velocity of diffusion is *inversely* as the root of the density.

The third column of figures shows the *calculated* diffusibility of the various gases on the law above enunciated; while the fourth column shows the *observed* diffusibility. These two series of numbers, it will be observed, agree very closely.

An inspection of this table informs us that 3.83 parts of hydrogen diffuse through a porous plate in the same time as one part of air; so that if the diffusion tube above described be filled with hydrogen, by the time the whole of this gas has diffused away only  $\frac{1}{3.83}$  parts of the same volume of air will have entered, thus causing the mercury to rise in the tube. If the gas in the diffusion tube is *heavier* than the air, it is clear that its volume will become *increased* by diffusion, because the lighter air enters with a greater velocity than the heavier gas escapes. Thus, if carbon dioxide be used 0.812 volumes of this gas (see table) escape, while one volume of air enters the tube; so that by the time the whole of the carbon dioxide has escaped, the volume of air in the tube will be increased to  $\frac{1}{0.812} = 1.23$  volumes.

**Problems in Diffusion.**—Problems involving the application of the foregoing principles are frequently given for solution. We shall now solve one of these.

100 cubic centimetres of carbon monoxide were allowed to diffuse into hydrogen, the pressure upon the gases remaining unaltered during the experiment. At the end of five minutes 20 cubic centimetres of hydrogen were found in the vessel containing the carbon monoxide. How many cubic centimetres of this latter gas had penetrated into the hydrogen?

Find, first of all, the density of carbon monoxide in the ordinary manner:— $\text{CO} = \frac{12+16}{2} = 14$ . Then,

$\sqrt{14} = 3.75$ . The velocity of diffusion is *inversely* as the root of the density; so that the velocity of diffusion of hydrogen is to the velocity of diffusion of carbon monoxide as 3.75 : 1. For every 3.75 parts of hydrogen, therefore, found in the vessel containing the carbon monoxide, one part of this latter gas has passed into the hydrogen. Now, 20 c.c. of hydrogen were found mixed with the carbon monoxide, so that the quantity of carbon monoxide penetrated into the hydrogen may be easily found :—

$$3.75 : 20 :: 1 : x = 5.34 \text{ cub. centim.}$$

**Summary.**—1. The volume occupied by the weight of an element proportional to its atomic weight is called the *atomic volume*.

2. The atomic volumes of most of the elements are equal to the atomic volume of hydrogen.

3. The volume occupied by the weight of an element or compound proportional to its molecular weight is called the *molecular volume*.

4. The molecular volumes of most of the elements and compounds are equal to the molecular volume of hydrogen. This is equivalent to saying that equal volumes of elementary and compound gases and vapours contain the same number of molecules.

5. A compound which, under the influence of heat, splits up into compounds of simpler composition is said to undergo *dissociation*.

6. All gases expand to nearly the same extent for an equal increment of temperature.

7. The coefficient of expansion of gases is .003665 for 1° C.

8. The volume occupied by a gas varies inversely as the pressure to which it is submitted.

9. Gases of different densities intermingle when separated from each other by a porous partition.

10. This property of intermixture takes place by virtue of a power called *diffusion*.

11. The velocity of diffusion of a gas varies inversely as the square root of its density.

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## CHAPTER V.

## THE CHEMISTRY OF THE HALOGEN ELEMENTS.

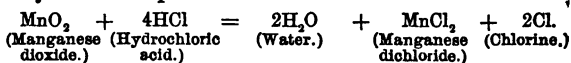
THE elements which are now about to occupy our attention form a natural group, the members of which possess many characters in common. The group is composed of the four elements chlorine, bromine, iodine, and fluorine, and these have received the name of *halogens*.<sup>1</sup>

13. CHLORINE.<sup>2</sup>

Symbol, Cl. Atomic weight, 35.5.

**Occurrence.**—The most abundant natural source of chlorine is common salt or sodium chloride, which exists in thick beds in Cheshire, Spain, and other parts of the world, as rock-salt. Sodium and potassium chlorides exist also in sea water, and potassium chloride is obtained in considerable quantities from the salt-beds of Stassfurt, in Prussia. Hydrogen chloride, or hydrochloric acid, has been detected in the gases evolved in volcanic regions. In combination with lead, mercury, and silver, chlorine exists in several well-known minerals.

**Preparation.**—Chlorine is generally prepared by heating manganese dioxide, a substance which we have already had occasion to mention in connection with oxygen (p. 39), with hydrochloric acid. The reaction may be thus represented:—



<sup>1</sup> *G. h-als*, the sea; *gēnnaō*, I produce. Applied because sea-salt (sodium chloride) is the type of the series of salts produced by these elements.

<sup>2</sup> *G. chloros*, greenish-yellow. Applied in consequence of the colour of the gas.

The apparatus used is shown in the accompanying figure:—

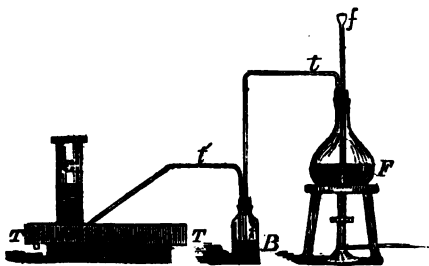


Fig. 20.—Preparation of chlorine.

The flask *F* is fitted with an india-rubber<sup>1</sup> cork perforated so as to receive a funnel-tube (*f*) which passes to the bottom of the flask, and a bent tube (*t*) which only just passes through the cork. The manganese dioxide being placed in the flask, hydrochloric acid is poured down the funnel, and a very gentle heat applied by means of the gas burner seen in the figure. The evolved gas rises through the tube *t*, and passes through the bottle *B*, which contains cold water, or, if the gas is required dry, sulphuric acid. This bottle serves to wash the gas, which then passes out through the tube *t'* into the vessel *G* standing on the shelf of the pneumatic trough *T*.

As chlorine is largely dissolved by cold water, and is moreover much heavier than the air, it may advantageously be collected by downward displacement, but if collected at the pneumatic trough *warm* water must be used. The apparatus for collecting chlorine by displacement must be so arranged as to prevent any of the gas escaping into the air, as it produces most dele-

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<sup>1</sup> Ordinary cork is rapidly destroyed by chlorine.

terious effects when inhaled. A convenient form of apparatus is figured below.

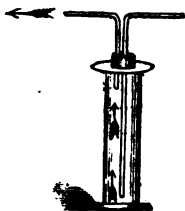
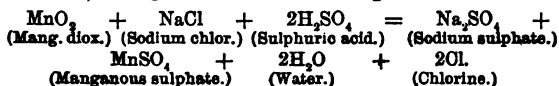


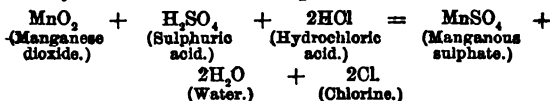
Fig. 21.  
Collection of chlorine by  
displacement.

A glass plate with a hole through its centre is fitted with an india-rubber cork and two bent tubes as shown in the figure. The escape gas is either sent into the open air or absorbed by some substance that forms an inodorous compound with it, such as sodium hydroxide (NaHO). The arrows show the direction of the gas.

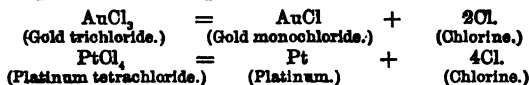
Chlorine may be also prepared by heating a mixture of common salt (sodium chloride), manganese dioxide, and sulphuric acid, thus:—



From the above equation we see that the *whole* of the chlorine is obtained in this decomposition. A similar result is obtained if sulphuric acid is mixed with the hydrochloric acid in the process first described:—



The chlorides of certain heavy metals, such as gold or platinum, decompose on heating, thus:—



Many other processes for preparing chlorine have been proposed; but into these the scope of the present manual will not permit us to enter.



**Properties.**—Chlorine is a greenish-yellow gas, having a most pungent and suffocating odour. It is fatal to animal life. Its density compared with hydrogen is 35.5, so that one litre weighs 35.5 criths, or  $35.5 \times .0896 = 3.18$  grammes. Compared with atmospheric air, its density is about 2.5, so that chlorine is one of the heaviest substances gaseous at ordinary temperatures. Under a pressure of  $8\frac{1}{2}$  atmospheres, at the ordinary temperature of the air, chlorine condenses to a yellow liquid having a specific gravity of 1.33. This liquid has never been solidified. Water at ordinary temperature dissolves about twice its volume of chlorine, forming a solution having the colour and odour of the gas. The quantity of gas dissolved is less when the water is warm; hence the use of warm water in the pneumatic trough when collecting this gas. Near the freezing point of water a definite *hydrate of chlorine* ( $\text{Cl} \cdot 5\text{H}_2\text{O}$ ) crystallises out from a solution of the gas in water.

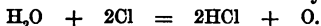
Chlorine cannot be made to combine *directly* with oxygen, although many oxides of chlorine are known. These, as we shall see presently, are all formed by indirect methods. With hydrogen and most of the metals<sup>1</sup> chlorine combines energetically, forming a series of compounds termed chlorides. A mixture of equal volumes of hydrogen and chlorine explodes on the application of a lighted taper—a volume of hydrochloric acid gas equal to that of the original mixture being produced. The combination of hydrogen and chlorine occurs also under the influence of light, slow combination taking place in diffuse daylight, and explosive combination occurring in direct sunlight or in the light of the electric arc. Chlorine supports the combustion of a taper, but it is only the hydrogen of the wax that burns: the carbon is deposited in dense

---

<sup>1</sup> For this reason the mercurial trough cannot be used for collecting the gas.

sooty clouds, making the flame look red and smoky. So great is the affinity of chlorine for hydrogen that a piece of paper wetted with warm turpentine ( $C_{10}H_{16}$ ) takes fire when plunged into the gas. Potassium and sodium burn brilliantly in chlorine when the heated metals are immersed in the gas.

Owing to its strong affinity for hydrogen, chlorine in presence of water acts as a powerful oxidiser, because it decomposes the water and liberates the oxygen:—



The oxygen at the moment of its liberation, or in the *nascent state*, is more energetic than free oxygen, and upon this depends the fact that chlorine is a powerful *bleaching* agent. Vegetable colouring matters in presence of chlorine and water become oxidised by this action into compounds possessing no colour, and are said to be *bleached*. A piece of cloth dyed with a vegetable colour may be kept in dry chlorine without undergoing any change of colour, but the addition of water soon discharges the colour. Chlorine acts likewise as a *disinfectant*,<sup>1</sup> its action upon the organic impurities in the air being probably similar to its action upon vegetable dyes, and depending upon the action of nascent oxygen liberated from water vapour, which, as we have previously learnt, is always present in the air.

Chlorine was discovered by Scheele in 1774, but it was first shown to be an element by Davy in 1810.

#### 1. COMPOUND OF CHLORINE WITH HYDROGEN.

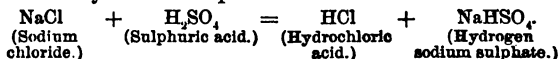
### 14. HYDROCHLORIC ACID.

Symbol, HCl. Molecular weight, 36.5.

**Preparation.**—We have just seen that hydrogen and chlorine combine directly to produce this substance.

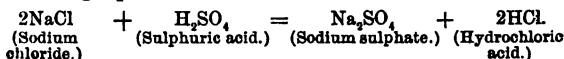
<sup>1</sup> L. *dis*, for *de*, from; *infectus*, from *inficio*, to pollute. A term applied to any material used for destroying polluting substances.

Hydrochloric acid is generally prepared by heating a mixture of common salt with sulphuric acid in a flask similar to that shown in Fig. 20. The reaction that occurs may be thus expressed:—

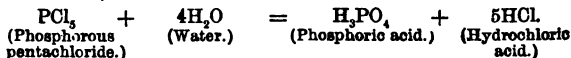
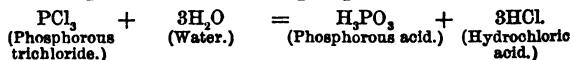


The gas is exceedingly soluble in water, so that it must be collected by displacement or over mercury.

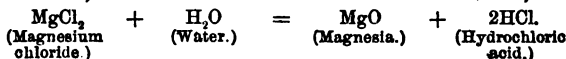
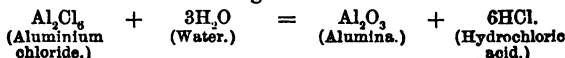
For preparing the acid on a large scale iron cylinders are employed, and twice as much salt as indicated in the foregoing equation. A stronger heat is applied than can be applied to the glass flask, and double the quantity of acid is given off, as will be seen in the following equation:—



Hydrochloric acid is also formed by the action of water upon the chlorides of phosphorus, thus:—



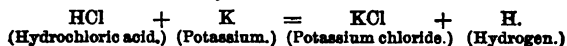
It is likewise produced when steam is passed over heated aluminium or magnesium chloride:—



Hydrochloric acid is found in volcanic gases, and also in certain rivers in South America, to the extent of  $\frac{1}{10}$  or  $\frac{2}{10}$  per cent., these rivers rising in volcanic formations.

**Properties.**—Hydrochloric acid is a colourless and transparent gas, having a most pungent and irritating

odour and a strongly acid taste. Its density referred to air is 1.27; referred to hydrogen it is  $\frac{35.5}{2} \div 1 = 18.25$ , so that one litre weighs 18.25 criths =  $18.25 \times .0896 = 1.64$  grammes. Hydrochloric acid is not combustible, neither does it support the combustion of a burning taper; but the metal potassium takes fire when heated in the gas, combining with the chlorine and liberating the hydrogen:—



At a temperature of  $10^{\circ}$ , under a pressure of 40 atmospheres, hydrochloric acid condenses to a colourless liquid which has not yet been solidified. Hydrochloric acid gas combines readily with water, one volume of water at the ordinary temperature of the air dissolving about 458 volumes of the gas. A bottle filled with the dry gas emits white fumes when the stopper is removed in moist air, owing to the condensation of the atmospheric moisture by the gas. When a bottle of the dry gas is opened under water, the water rushes in with almost explosive violence. The solution of the gas in water is the *muriatic acid*<sup>1</sup> of commerce. It usually contains about 32.6 per cent. of real HCl, and has a specific gravity of 1.16: the *saturated solution*<sup>2</sup> of the gas has a specific gravity of 1.21, and contains about 42.4 per cent. of HCl. The pure acid is colourless; but the crude acid of commerce is always yellow from the presence of iron and other impurities.

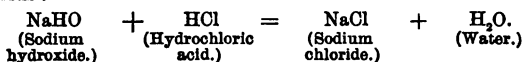
A strong solution of hydrochloric acid fumes always in the air, owing to the escape of small quantities of the gas. When boiled in a retort, the dissolved gas continues to be given off till there remains a liquid which distils under ordinary atmospheric pressure at

<sup>1</sup> L. *mūria*, brine.

<sup>2</sup> A saturated solution is a solution which has taken up its maximum quantity of the dissolved substance.

110°, and which contains 20·22 per cent. of HCl. Under diminished pressure this constant boiling point is reached at a lower temperature; and it has been found by Prof. Roscoe that the percentage of HCl in such liquids of constant boiling point varies with every alteration of boiling point, so that they cannot be considered as definite chemical compounds of HCl and water. A similar fact has been observed with respect to other aqueous acids. Thus the nitric acid, which boils constantly under the ordinary atmospheric pressure at 190·5°, contains 68 per cent. of HNO<sub>3</sub>. (See p. 59.)

Hydrochloric acid is decomposed by many metals with the formation of a metallic chloride and the liberation of hydrogen, as we have already seen (p. 35). A similar decomposition occurs in presence of metallic *hydroxides*, water being formed instead of hydrogen. Thus:—



In presence of certain oxides, such as manganese dioxide, decomposition occurs, as we have already had occasion to notice, with liberation of chlorine. This reaction occurs also if dry hydrochloric acid gas is passed over the heated oxide. Hydrochloric acid combines with ammonia gas, forming white fumes of ammonium chloride:—



A glass rod dipped in hydrochloric acid is thus often used as a test for the presence of ammonia.

Hydrochloric acid is decomposed by a current of electricity, equal volumes<sup>1</sup> of hydrogen and chlorine being evolved. The aqueous acid is known also by the

---

<sup>1</sup> The chlorine does not begin to be given off in its proper quantity till the solution is saturated with it, the first portions being dissolved by the water.

trivial names of *marine acid* and *spirit of salt*. The gas was discovered by Priestly in 1772.

**15. NITRO-HYDROCHLORIC ACID.**—A mixture of nitric and hydrochloric acids is known by this name, and also by the name of *agua-regia*, because it dissolves the noble metals gold, platinum, &c. These metals do not dissolve in either acid by itself, but the mixed acids attack them slowly in the cold and rapidly when heated, the respective chlorides being produced. The action upon the metals depends upon the liberation of chlorine from the hydrochloric acid by the withdrawal of its hydrogen by the powerfully oxidising nitric acid.

## 2. OXIDES AND OXYGEN ACIDS OF CHLORINE.

It has already been mentioned that chlorine cannot be made to combine *directly* with oxygen; nevertheless three oxides have been obtained by indirect means. These are—

Chlorine monoxide .....	$\text{Cl}_2\text{O}$ .
Chlorine trioxide .....	$\text{Cl}_2\text{O}_3$ .
Chlorine tetroxide .....	$\text{Cl}_2\text{O}_4$ .

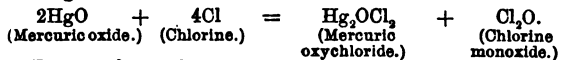
The following acids are also known :—

Hypochlorous acid .....	$\text{HClO}$ .
Chlorous acid .....	$\text{HClO}_2$ .
Chloric acid .....	$\text{HClO}_3$ .
Perchloric acid .....	$\text{HClO}_4$ .

## 16. CHLORINE MONOXIDE.

Symbol,  $\text{Cl}_2\text{O}$ . Molecular weight, 87.

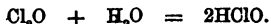
**Preparation.**—By passing chlorine over mercuric oxide<sup>1</sup> contained in a glass tube cooled by ice. The following reaction occurs :—



**Properties.**—Chlorine monoxide is a pale yellowish gas having a powerful and peculiar odour. It decom-

<sup>1</sup> The oxide must be prepared by precipitation for this purpose.

poses explosively on a slight elevation of temperature, and sometimes spontaneously. When cooled by a mixture of ice and salt the gas condenses into a deep orange-red explosive liquid. When chlorine monoxide is passed into water it forms hypochlorous acid, thus:—



For this reason it is sometimes called hypochlorous anhydride.<sup>1</sup> Chlorine monoxide can indeed be obtained from its corresponding acid by treating the acid with phosphorous pentoxide, a substance possessing a great affinity for water:—

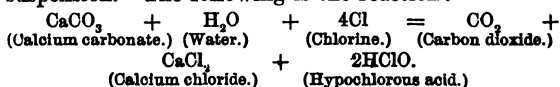


It will be now advantageous to consider this acid.

## 17. HYPOCHLOROUS ACID.\*

Symbol,  $\text{HClO}$ . Molecular weight, 52.5.

**Preparation.**—It has just been mentioned that this acid may be produced by dissolving the anhydride in water. Another obvious method of preparation is to pass chlorine into water containing mercuric oxide in suspension. It is produced also by passing chlorine into water containing calcium carbonate (chalk) in suspension. The following is the reaction:—

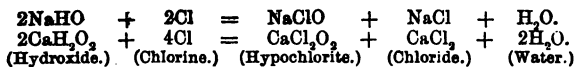


When chlorine is passed into water containing in suspension or solution certain hydroxides—such as those of sodium or calcium—hypochlorites are formed:—

<sup>1</sup> G. *an*, without; *h-udör*, water.

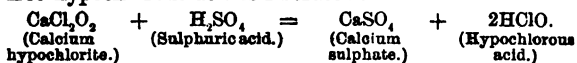
<sup>2</sup> The sign — is used in its ordinary algebraic sense.

<sup>3</sup> The student may be here again reminded of the meaning of the prefixes *hypo*, signifying *under*, and *per*, signifying *over*. The *hypochlorous* acid contains one atom of oxygen *less* than chlorous acid, and the *perchloric* acid contains one atom of oxygen *more* than chloric acid.

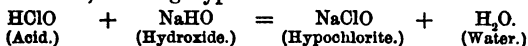


The compound produced by passing chlorine over slaked lime does not appear to be a hypochlorite. This compound, called *bleaching powder*, will be considered subsequently.

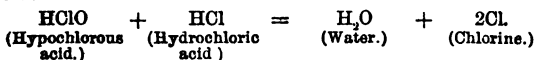
By treating a hypochlorite with some stronger acid free hypochlorous acid is liberated :—



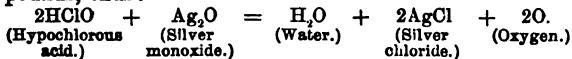
**Properties.**—The aqueous solution has an acid taste, a yellow colour, and a sweetish odour. Like chlorine, it possesses powerful bleaching properties, and acts as a strong oxidising agent. The acid combines with hydroxides, forming hypochlorites :—



Hypochlorous acid is decomposed by boiling, and also by hydrochloric acid, the chlorine of both acids being liberated. In preparing hypochlorous acid from a hypochlorite, it is not, therefore, advisable to use hydrochloric acid. The reaction that occurs is as follows :—



Decomposition occurs also in presence of silver monoxide, the oxygen being evolved from both compounds, thus :—



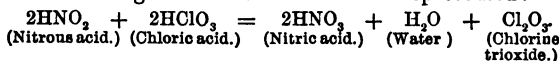
## 18. CHLORINE TRIOXIDE.

Symbol,  $\text{Cl}_2\text{O}_3$ . Molecular weight, 119.

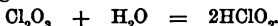
**Preparation.**—This substance is prepared by depriving chloric acid (to be considered presently) of some of its oxygen by means of nitrous acid. It has already been mentioned (see p. 56) that nitrous acid may be prepared by depriving nitric acid of some of its



oxygen by means of arsenic trioxide: in practice, therefore, these reactions are combined, and chlorine trioxide is obtained by gently heating a mixture of potassium chlorate, nitric acid, and arsenic trioxide.<sup>1</sup> The final stage of the reaction is thus represented:—



**Properties.**—A yellowish-green gas, condensing, when pure, into a deep red-brown liquor on exposure to the cold, produced by a mixture of ice and salt. Its density referred to hydrogen is  $(35.5 \times 2) \div (16 \times 3) = 59.5$ ; so that 1 litre weighs 5.33 grammes. It unites with water, forming chlorous acid:—

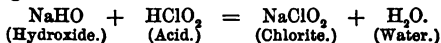


Chlorine trioxide may be thus regarded as the anhydride of chlorous acid.

## 19. CHLOROUS ACID.

Symbol,  $\text{HClO}_2$ . Molecular weight, 68.5.

**Preparation and Properties.**—This acid is prepared in the manner just described, viz., by dissolving the anhydride in water. It is a golden-yellow liquid, possessing 14 times the bleaching power of chlorine water. The aqueous acid decomposes on heating to  $50^\circ$ , chloric and hydrochloric acids, together with free chlorine, being produced. It unites with certain hydroxides, forming a series of salts called *chlorites*:—

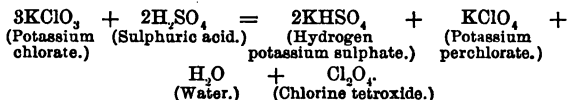


## 20. CHLORINE TETROXIDE.

Symbol,  $\text{Cl}_2\text{O}_4$ . Molecular weight, 135.

**Preparation and Properties.**—This gas is prepared by the action of sulphuric acid on potassium chlorate:—

<sup>1</sup> Tartaric acid, or, still better, cane-sugar, may be used instead of the arsenic trioxide.



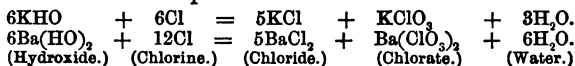
The chlorate must be made into a paste with the acid, and heated in warm water in a glass retort in small portions at a time.

Chlorine tetroxide is a gas of a deep yellow colour, and possessing a powerful odour quite distinct from that of chlorine. It dissolves in water, giving a solution which bleaches; and it liquefies when exposed to great cold. At a temperature below the boiling point of water this gas decomposes with explosive violence. A mixture of potassium chlorate and sugar bursts into flame when touched by a rod dipped in sulphuric acid, owing to the liberation of this gas, the carbon of the sugar<sup>1</sup> burning at the expense of the oxygen of the chlorate. The aqueous solution of this oxide does not yield salts of a corresponding acid.

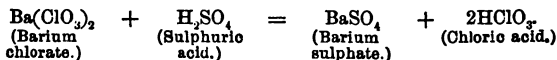
## 21. CHLORIC ACID.

Symbol,  $\text{HClO}_3$ . Molecular weight, 84.5.

**Preparation.**—When chlorine is passed into hot water<sup>2</sup> containing certain hydroxides in solution or in suspension chlorates are produced as follows:—



From barium chlorate chloric acid is prepared by adding sulphuric acid in just sufficient quantity to combine with the barium:—



<sup>1</sup> The formula of cane-sugar is  $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ .

<sup>2</sup> It will be remembered that the *cold* solution produces a *hypochlorite* (see p. 92). When boiled the hypochlorite is decomposed into a *chlorate*.

The insoluble barium sulphate is removed by filtration<sup>1</sup> and the liquid concentrated by evaporation *in vacuo*.

**Properties.**—A clear syrupy acid liquid, giving off a pungent odour when warm. Chloric acid decomposes rapidly at a boiling heat, and also in presence of hydrochloric acid. It is a powerful oxidiser, charring organic substances,<sup>2</sup> sometimes even with ignition. The chlorates, as we have already seen (p. 39), give off oxygen when heated. By subtracting water from chloric acid we obtain, theoretically, the following oxide:—

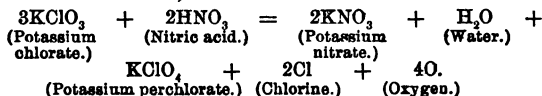


This pentoxide has, however, not yet been obtained.

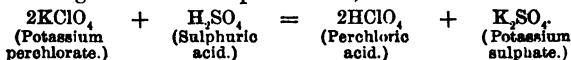
## 22. PERCHLORIC ACID.

Symbol,  $\text{HClO}_4$ . Molecular weight, 100.5.

**Preparation.**—By throwing potassium chlorate in small portions into nitric acid kept boiling in a retort, potassium perchlorate is formed and oxygen and chlorine liberated, thus:—



Perchloric acid may be obtained from its salts by treating these with sulphuric acid, thus:—



**Properties.**—Pure perchloric acid is a colourless volatile liquid forming a white crystalline *hydrate*

<sup>1</sup> Filtration in chemical operations is generally effected by passing the liquid through unsized paper, such as blotting-paper. A circular piece of the paper is first folded along its diameter and then again at right angles to the former direction, so as to form a quadrant. This, when opened, makes a cone, which is fitted into a glass funnel and wetted with water before using.

<sup>2</sup> Organic substances invariably contain carbon.

with water ( $\text{HClO}_4 \cdot \text{H}_2\text{O}$ ). It is one of the most powerful oxidising agents known: when brought in contact with organic substances, violent and explosive combustion immediately occurs. It undergoes decomposition when heated, and even at the ordinary temperature when kept for some time. When the hydrogen of this acid is replaced by metals, a series of salts termed perchlorates is formed. The perchlorates, like the chlorates, give off their oxygen when heated. The heptoxide corresponding to this acid ( $\text{Cl}_2\text{O}_7$ ) has not yet been obtained.

### 3. COMPOUND OF CHLORINE WITH NITROGEN.

Chlorine forms one compound with nitrogen, but this, owing to the great danger attending its manipulation, has not been much studied. It was formerly considered the trichloride ( $\text{NCl}_3$ ), but recent researches have tended to show that it contains hydrogen. This compound is prepared by passing chlorine gas in excess into aqueous ammonia. It is a yellow oily liquid of a most penetrating odour, and possesses great explosive properties, detonating<sup>1</sup> with extraordinary violence when heated, or even when touched with any greasy substance.

### 4. COMPOUNDS OF CHLORINE WITH NITROGEN AND OXYGEN.

It has been previously explained that a mixture of nitric and hydrochloric acids (aqua-regia) dissolves gold and platinum, this solvent action depending on the liberation of chlorine from the hydrochloric acid. In addition to chlorine, the two following compounds are evolved when the mixed acids are heated:—

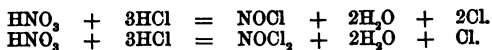
$\text{NOCl}$  .....Nitrogen oxychloride, or chloronitrous gas.

$\text{NOCl}_2$ .....Nitrogen oxy-dichloride, or chloronitric gas.

The following equations represent the respective reactions:—

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<sup>1</sup> L. *détôno*, to thunder.



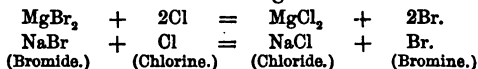
Both substances are yellowish gases, which may be condensed to liquids by a freezing mixture. They are also obtained by the direct union of nitrogen dioxide and chlorine.

### 23. BROMINE.<sup>1</sup>

Symbol, Br. Atomic weight, 80.

**Occurrence.**—This element, like chlorine, always occurs in combination. It is found in small quantities in sea water, and in the waters of many salt-springs, as magnesium bromide. It occurs also in the ash of seaweed, and as silver bromide is found native in Mexico, Chili, and Bretagne.

**Preparation.**—The liquors containing the bromine salts are evaporated, so as to remove the less soluble salts, which crystallise out first. Through the remaining liquid, or *mother-liquor* as it is called, a stream of chlorine is then passed, and this liberates the bromine in accordance with the following reactions:—



The liquid is then shaken up with ether,<sup>2</sup> which dissolves the bromine, forming a beautiful red solution, which separates as a distinct layer on standing. This layer of ethereal solution of bromine is separated and agitated with an aqueous solution of sodium hydroxide, which unites with the bromine, forming sodium bromide and bromate, just in the same manner as chlorine forms, under similar conditions, sodium chloride and chlorate (see p. 95). The ether can be recovered by distillation, and the solution is evaporated to dryness and ignited at a red heat, so as to convert the bromate into bromide,

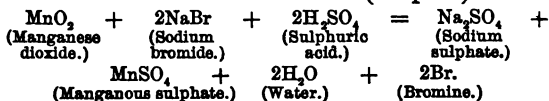
<sup>1</sup> G. bröms, a stink.

<sup>2</sup> The ordinary sulphuric ether of commerce.

the reaction being analogous to that which occurs when oxygen is prepared from potassium chlorate (see p. 39):—



The bromide is then distilled in a retort with manganese dioxide and sulphuric acid, when the bromine is liberated and passes over into the receiver, which must contain cold water. The reaction that occurs at this stage is analogous to that which occurs in the preparation of chlorine from common salt (see p. 85):—



The ash of sea-weed contains also iodine, so that in preparing bromine from this source a slightly different process is used.

**Properties.**—Bromine is a heavy liquid of a deep red colour and possessing a most irritating and repulsive odour. It is very volatile even at ordinary temperatures, so that a drop let fall on to a plate soon disappears. The liquid itself gives off deep red-brown suffocating vapours whenever exposed to the air. The specific gravity of the liquid is 2·976, and that of the vapour referred to air is 5·54. Referred to hydrogen its density is, in conformity with the law already enunciated (see p. 61), equal to its atomic weight, viz., 80; consequently 1 litre weighs  $80 \times 0\cdot0896 = 7\cdot17$  grammes. At  $-22^\circ$  bromine solidifies to a hard, brittle mass of a blackish colour, which does not become liquid again till about  $-12^\circ$ . The liquid boils under ordinary atmospheric pressure at  $63^\circ$ . Bromine dissolves in water, forming a reddish-brown solution which possesses the characteristic odour of the element itself; and this solution, like chlorine-water, acts as a powerful bleaching agent. The amount of bromine dissolved by water varies, within certain small limits, with the temperature

of the water; at the ordinary temperature of the air bromine-water contains about 3.226 per cent. of bromine. At the freezing point of water bromine-water deposits a solid *hydrate* analogous in composition to the chlorine hydrate ( $\text{Br} \cdot 5\text{H}_2\text{O}$ ).

Bromine colours starch orange-yellow, this reaction serving as a test for the presence of this element. Bromine is freely dissolved by carbon disulphide ( $\text{CS}_2$ ) and by many organic liquids, such as ether ( $\text{C}_4\text{H}_{10}\text{O}$ ) and chloroform ( $\text{CHCl}_3$ ).

In its chemical characters bromine closely resembles chlorine, although it does not possess such powerful affinities as this latter element. We have just had occasion to mention that chlorine displaces bromine from its combination with the metals (see p. 98). Under certain conditions, however, bromine can be made to displace chlorine, as when perbromic acid ( $\text{HBrO}_4$ ) is obtained by the action of bromine on perchloric acid. Bromine possesses a strong affinity for hydrogen, the two elements uniting at a red heat or in the sunlight, but the union is not so energetic as in the case of chlorine and hydrogen. The affinity for hydrogen is, however, sufficiently great to enable bromine to decompose water when a mixture of steam and bromine vapour is passed through a tube heated to bright redness. Chlorine, as we know, exerts a similar decomposition (see p. 26), the reaction being analogous:—



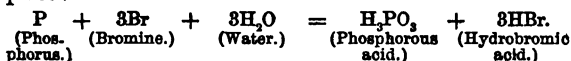
A lighted taper does not, however, continue to burn in bromine vapour. Bromine can be made to unite directly or indirectly with all the elementary bodies. In some cases the union is very energetic—arsenic and antimony, for instance, taking fire and burning brilliantly when thrown into the vapour or liquid. Bromine was discovered by Balard in 1826.

## 1. COMPOUND OF BROMINE WITH HYDROGEN.

## 24. HYDROBROMIC ACID.

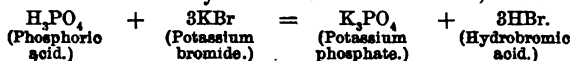
Symbol, HBr. Molecular weight, 81.

**Preparation.**—The method by which hydrobromic acid can be prepared by the direct union of its elements has just been indicated. Most of the processes given for obtaining hydrochloric acid yield hydrobromic acid when a bromide is substituted for a chloride. In practice, however, it is found most convenient to act on the tribromide of phosphorus with water (compare the action of the *chloride* of phosphorus, p. 88), or, what comes to the same thing, to drop bromine into water containing phosphorus.<sup>1</sup> The following reaction takes place:—

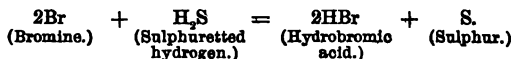


Other processes yielding this acid may be now briefly noticed.

When phosphoric acid is heated with potassium or sodium bromide the hydrobromic acid is liberated, thus:—



By passing sulphuretted hydrogen gas through bromine-water this acid is also obtained:—



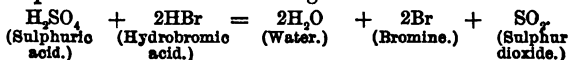
**Properties.**—Like hydrochloric acid, a colourless and transparent gas of a pungent odour and acid taste. It is very soluble in water, the aqueous solution when concentrated boiling, under 760 mm. pressure, at 126° and containing 47·8 per cent. of HBr. The saturated solution has a density of 1·29, and fumes in the air. The gas liquefies at — 69° and solidifies at — 73°. The

<sup>1</sup> That modification of phosphorus known as “amorphous phosphorus” is the most advantageous for this purpose.



density of hydrobromic acid referred to hydrogen is, calculated in the ordinary way,  $\frac{80.5}{2} = 40.5$ . Referred to air the density is 2.806.<sup>1</sup>

From what has been previously said concerning atomic and molecular volumes, the student will perceive that hydrobromic acid should contain half its volume of hydrogen. To prove this it is only necessary to heat a fragment of potassium in a measured portion of the dry gas, when the bromine combines with the metal and a volume of hydrogen equal to half the volume of the original gas is liberated. Hydrobromic acid is immediately decomposed by chlorine with liberation of its bromine. It is also decomposed by sulphuric acid in the following manner :—



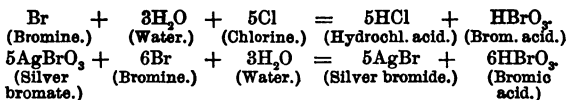
Hence, sulphuric acid cannot be advantageously used to liberate hydrobromic acid from a bromide.

## 2. OXIDES AND OXYGEN ACIDS OF BROMINE.

This series of compounds is by no means so complete as the corresponding series of chlorine compounds. Bromine monoxide ( $\text{Br}_2\text{O}$ ) is stated to be formed when bromine-vapour is passed over dry mercury oxide and the corresponding acid; hypobromous acid is obtained by the action of mercury oxide on bromine-water. There is no necessity for representing the equations, as the reactions are, in these cases, analogous to those of chlorine under similar conditions.

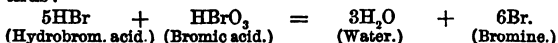
**25. BROMIC ACID ( $\text{HBrO}_3$ ).**—This acid is prepared by methods analogous to those given for preparing chloric acid; also by passing chlorine through bromine-water, or by acting on silver bromate with bromine in presence of water :—

<sup>1</sup> The density of hydrogen referred to air is .0693, so that when the density of a gas referred to hydrogen is known, it is only necessary to multiply this number by .0693 to obtain the density referred to air.



The bromates are very similar in appearance and properties to the chlorates, and can be obtained by analogous methods. The bromates of potassium and sodium can be most advantageously prepared by saturating a solution of the carbonates ( $\text{K}_2\text{CO}_3$  or  $\text{Na}_2\text{CO}_3$ ) with chlorine and then adding bromine. This is another instance in which bromine displaces chlorine. The bromates, when heated, decompose in some cases into bromide and oxygen, and in other cases into oxides, bromine, and oxygen.

Hydrobromic acid is decomposed by bromic acid, thus:—



The anhydride  $\text{Br}_2\text{O}_5$  is not known.

**26. PERBROMIC ACID.**—This acid is obtained by adding bromine to perchloric acid and evaporating the solution at a gentle heat. It is a syrupy, colourless liquid, and forms a series of salts termed *perbromates*. The anhydride  $\text{Br}_2\text{O}_7$  is unknown.

Bromine unites with chlorine, forming a volatile reddish-yellow liquid, which gives off strongly-smelling vapours. The exact composition of this chloride has not yet been ascertained. A nitrogen bromide also exists, and is formed by the action of potassium bromide upon nitrogen chloride. It is a reddish-black, volatile, oily liquid, possessing violent explosive properties.

## 27. IODINE.<sup>1</sup>

Symbol, I. Atomic weight, 127.

**Occurrence.**—This element occurs, in combination with potassium and sodium, in sea water and in the

<sup>1</sup> G. *iodes*, violet-coloured; applied in consequence of the colour of the vapour.

water of many mineral springs. It is assimilated<sup>1</sup> by marine plants and by many marine animals; the former source yielding all the iodine used. Mercury and silver iodides are found in the native state as minerals.

**Preparation.**—Sea-weeds are collected and burnt to ashes in shallow pits. This ash, or *kelp*, is then treated with hot water, and the solution evaporated so as to remove the less soluble salts. The mother-liquor is then distilled in a leaden retort with sulphuric acid and manganese dioxide; the iodides of sodium and magnesium being thereby decomposed in a manner analogous to the decomposition of sodium chloride or bromide when treated with these same reagents. (See pp. 85 and 99.)

**Properties.**—Iodine is a dark grey crystalline solid with a metallic lustre. It melts at  $115^{\circ}$  and boils at about  $200^{\circ}$ , giving off a beautiful violet vapour. At ordinary temperatures it is always giving off small traces of vapour, a bottle containing the solid always showing a violet colour when held up to the light. The specific gravity of the solid is 4.95, and of the vapour 8.801, referred to air, or 127 referred to hydrogen. It possesses an odour somewhat resembling that of chlorine, but much fainter, and dissolves but sparingly in water, though readily in water containing in solution a soluble iodide, ammonium chloride, &c. It dissolves also in alcohol (spirits of wine) and ether, forming brownish-red solutions, and in carbon disulphide and chloroform, forming rich violet solutions. Iodine produces a splendid blue colour with starch; this reaction serving as a test by means of which a very small trace of the elements can be detected. As iodine is liberated from its compounds by chlorine, the test is applied by first adding starch paste to the liquid to be tested, and then a drop of chlorine water.

In its chemical characters iodine is less active than

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<sup>1</sup> *L. assimilo*, to convert to the nature of another thing.

chlorine or bromine, being displaced from its compounds by both these elements. When iodine is brought into contact with phosphorus, combination instantly occurs, and the phosphorus takes fire. Iodine combines directly with many of the metals and with hydrogen under certain conditions, but does not, like chlorine and bromine, decompose water at a red heat. Iodine was discovered by Courtois in 1812.

#### 1. COMPOUND OF IODINE WITH HYDROGEN.

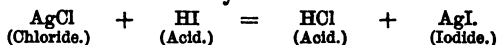
#### 28. HYDRIODIC ACID.

Symbol, HI. Atomic weight, 128.

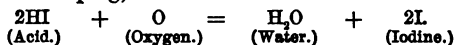
**Preparation.**—Hydrogen and iodine combine directly when passed through a red-hot tube, and at a lower temperature in presence of platinum in a finely-divided state. As all the reactions that yield hydrobromic acid yield hydriodic acid when an iodide or iodine is substituted for a bromide or bromine, it will be unnecessary to repeat these actions here. In practice, the acid is generally prepared by acting on phosphorus tri-iodide with water (compare reactions of bromine and chlorine, pp. 88 and 101), or by passing a stream of sulphuretted hydrogen gas through water containing iodine in suspension (compare bromine reaction, p. 101). If the gaseous acid is required, the phosphorus (amorphous) may be introduced into a retort and just covered with water. The iodine is then added in small portions, and heat applied, when a regular stream of the gas is evolved.

**Properties.**—Hydriodic acid is at ordinary temperatures a colourless, strongly acid gas, fuming in the air and very soluble in water. It liquefies under pressure and solidifies at  $-55^{\circ}$ . Its density referred to hydrogen is 64. The aqueous acid yields on distillation an acid boiling constantly at  $127^{\circ}$  under a pressure of 774 mm., and containing 57 per cent. of HI. The specific gravity of the saturated solution of the acid is 2.0.

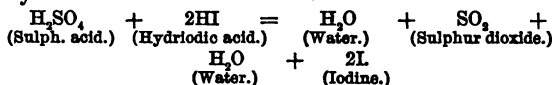
Hydriodic acid is instantly decomposed by chlorine and bromine, with the liberation of iodine and the formation of hydrochloric or hydrobromic acid. Under certain conditions, however, the iodine in hydriodic acid may be made to displace chlorine, as when silver chloride is heated with hydriodic acid:—



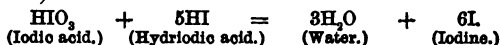
In organic chemistry we shall meet with other cases in which iodine displaces chlorine. Hydriodic acid is decomposed by heat alone, the amount of iodine liberated depending on the temperature, pressure, and extent of heated surface. The hydrogen of hydriodic acid is easily removed by oxidising agents; so that this acid is often used for abstracting oxygen from organic compounds. Oxygen readily decomposes hydriodic acid at a red heat when a mixture of the two gases is passed through a red-hot tube, water and iodine being the results of the decomposition. Even at ordinary temperatures an aqueous solution of the acid becomes brown on keeping, from the liberation of iodine:—



Hydriodic acid is decomposed by sulphuric acid in the same manner as hydrobromic acid, so that sulphuric acid cannot be used for the preparation of hydriodic acid from an iodide:—



Iodic acid decomposes hydriodic acid (compare decomposition of hydrobromic acid by bromic acid, p. 103):—



Certain metals—such as potassium, zinc, mercury, and iron—liberate the hydrogen from hydriodic acid:—



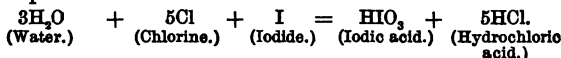
In presence of metallic oxides and hydroxides, hydriodic, like hydrochloric and hydrobromic acids, forms an iodide and water. (See p. 90 for reaction.)

## 2. OXIDES AND OXYGEN ACIDS OF IODINE.

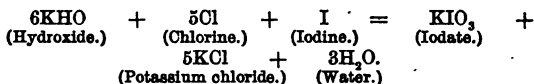
The most important of the oxides and acids of iodine are as follow :—

<i>Oxide.</i>	<i>Corresponding acid.</i>
Iodine pentoxide, $I_2O_5$ .	Iodic acid, $HIO_3$ .
Iodine heptoxide, $I_2O_7$ .	Periodic acid, $HIO_4$ .

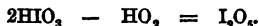
**29. IODIC ACID AND ANHYDRIDE.**—This acid may be prepared by oxidising iodine with boiling nitric acid, evaporating to dryness and crystallising the crude acid from an aqueous solution. It may be also obtained by passing chlorine through water in which iodine is suspended :—



In a similar manner an iodate is formed when iodine is dissolved in sodium or potassium hydroxide and water, and chlorine passed through the solution. The whole of the iodine is in this reaction converted into iodate, as is made manifest by the following equation :—



Iodic acid is a crystalline solid which resembles chloric and bromic acid in most of its chemical characters. At  $200^\circ$  the acid gives off the elements of water, leaving the anhydride or iodine pentoxide :—



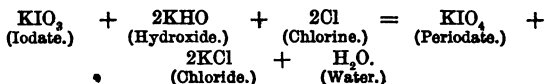
The pentoxide is likewise a white crystalline solid, having a specific gravity of 4.25. It dissolves in water, forming the acid, and at a high temperature is decomposed into iodine and oxygen.

The iodates decompose on heating in a similar manner to the chlorates and bromates.

**30. PERIODIC ACID AND ANHYDRIDE.**—This acid is obtained by acting on perchloric acid with iodine, thus furnishing another instance of the displacement of chlorine by iodine:—



The periodates of potassium and sodium are formed by passing chlorine through solutions of the iodates of these metals in presence of the corresponding hydroxides:—



(The reaction is in reality more complex than the above, owing to the tendency of the periodates to unite with other salts, water, &c.; but for the present the student may consider this equation as representing the true changes undergone.)

Periodic acid is a white crystalline solid, melting at  $130^\circ$ , and decomposing at  $170^\circ$  into water and the anhydride or iodine heptoxide. The metallic periodates are decomposed by heat, some into oxygen and iodides, others into a mixture of iodide and oxide and free oxygen.

Iodine unites directly with chlorine in several proportions, the most important of these compounds being the monochloride ( $\text{ICl}$ ) and the trichloride ( $\text{ICl}_3$ ). The former compound is a red-brown oily liquid of a most pungent odour. At low temperatures it is a yellow crystalline solid. The trichloride is an orange-yellow crystalline substance which melts at about  $20^\circ$ . Iodine unites with bromine, forming a crystalline compound and also a dark-brown liquid. When iodine acts on aqueous ammonia, an iodide of nitrogen is produced as a black insoluble powder, which, when dry, is highly explosive.

### 31. FLUORINE.<sup>1</sup>

Symbol, F. Atomic weight, 19.

**Occurrence.**—This element has a wide distribution in nature, but is not found in large quantities. Its most abundant source is fluor-spar (calcium fluoride), a mineral found in Derbyshire: it is found also in considerable quantities in *cryolite* (a compound of aluminium fluoride with sodium fluoride), a mineral occurring in Greenland. Fluorine is likewise found in minute traces in many other minerals; in bones, teeth, and blood of animals; in many plants; and in certain mineral springs.

**Preparation.**—It is extremely doubtful whether fluorine has ever been prepared in the pure state: so great is its chemical activity that it decomposes the material of almost any vessel in which its isolation is attempted. By acting on silver fluoride with iodine or chlorine in a vessel of fluor-spar, or in a sealed glass tube, a colourless gas is obtained which has been regarded as fluorine.

#### 1. COMPOUND OF FLUORINE WITH HYDROGEN.

### 32. HYDROFLUORIC ACID.

Symbol, HF. Molecular weight, 20.

**Preparation.**—This acid may be prepared by distilling a mixture of fluor-spar with sulphuric acid in a retort of lead or platinum, as glass is rapidly corroded by it. The form of the retort is shown in Fig. 22.

Powdered fluor-spar is mixed with twice its weight

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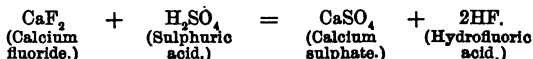
<sup>1</sup> From *fluor*, spar; so called because this mineral is sometimes used as a *flux*—that is, as a substance to facilitate the fusion of mineral substances. (L. *fluo*, I flow.)





Fig. 22.  
Hydrofluoric acid retort and condenser.

of strong sulphuric acid, and the mixture gently heated in the retort. The U-shaped condenser is immersed in a freezing mixture, and the acid liquefies as it comes over. The reaction is as follows :—



Dry hydrofluoric gas is prepared by heating the double fluoride of potassium and hydrogen ( $\text{KHF}_2$ ) to redness in a platinum vessel, when it splits up into  $\text{HF}$  and  $\text{KF}$ .

**Properties.**—Hydrofluoric acid is a colourless gas of a strongly acid character, which fumes in moist air and is readily absorbed by water. The liquid condensed in the U-tube of the above apparatus is a strong aqueous acid requiring a temperature of  $-20^\circ$  for its liquefaction. This strong acid unites with water with a hissing sound, and when dropped upon the skin produces a painful ulcer. In dealing with the acid great care should be taken not to inhale the vapours, as, from their highly corrosive nature, they are very dangerous. The solution of hydrofluoric acid in water has been found by Roscoe to attain a constant boiling point under ordinary atmospheric pressure when the liquid contains 37 per cent. of  $\text{HF}$ .

The most remarkable property of hydrofluoric acid is its corrosive action upon glass: the reason of this action we shall be better enabled to study when we have made ourselves acquainted with the element silicon. Hydrofluoric acid dissolves many of the metals, with the formation of a fluoride and the liberation of

hydrogen. In the case of potassium the action becomes explosive.

No compound of fluorine with oxygen has hitherto been obtained.

**Summary.**—1. The elements chlorine, bromine, iodine, and fluorine form a natural group, termed the *halogens*.

2. These elements form hydrogen acids, consisting of one volume of the element united with one volume of hydrogen *without condensation*.

3. Chlorine, bromine, and iodine are liberated from their compounds with metals by acting on a chloride, bromide, or iodide with sulphuric acid and manganese dioxide.

4. Hydrochloric acid is generally prepared by heating common salt (sodium chloride) with sulphuric acid. Hydrobromic acid is usually obtained by acting on phosphorus with bromine in presence of water. Hydriodic acid is best prepared by passing sulphuretted hydrogen gas through water containing iodide in suspension. Hydrofluoric acid is prepared by heating a fluoride (usually calcium fluoride) with sulphuric acid.

5. By indirect means, chlorine, bromine, and iodine may be made to unite with oxygen and with oxygen and hydrogen, forming a series of oxides and oxacids. Fluorine has not yet been made to combine with oxygen.

6. Compounds of chlorine, bromine, and iodine with nitrogen have been obtained by acting on ammonia with these elements respectively.

7. Chlorine, bromine, and iodine exhibit a gradation in atomic weight, physical properties, and chemical energy.

8. Chlorine displaces bromine and bromine iodine from many of its compounds, but in certain cases iodine may be made to displace bromine and bromine chlorine.

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## CHAPTER VI.

## CARBON AND SILICON.

THESE two elements—like chlorine, bromine, iodine, and fluorine—are closely allied in their chemical characters. To the study of this group we may now pass.

33. CARBON.<sup>1</sup>

Symbol, C. Atomic weight, 12.

**Occurrence.**—Carbon is one of the most abundant and widely distributed of the elements. It occurs in nature in the free state, and in large quantities in combination with oxygen and metals as carbonates; chalk or calcium carbonate being the most abundant. This last-mentioned compound contains 12 per cent. of carbon. Carbon is an essential constituent of all organic compounds: organic chemistry has, indeed, been defined as *the chemistry of the carbon compounds*.

Carbon exists in several modifications, of which the three most important are the following:—

1. **DIAMOND.**—This valuable gem consists of nearly pure carbon in a crystalline form, and is found in India, Brazil, Borneo, the Urals, and South Africa. The specific gravity of the diamond is 3.55, and it is the hardest known substance, being capable of scratching all other minerals. It is this great hardness which makes the diamond so valuable for cutting and writing upon glass. The diamond in its purest form is colourless, lustrous, and transparent; but some specimens exhibit slight tints of yellow, green, red, brown, or black. Like carbon in all its forms, the diamond cannot be melted by the heat of the most powerful furnace, but when heated to the intense temperature of the electric arc, it swells

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<sup>1</sup> L. *carbo*, coal.

up and becomes a black coke-like mass. The combustibility of the diamond was predicted by Newton, and was first effected by the Florentine Academicians in 1694 by placing the gem in the focus of a large concave mirror. When strongly heated in oxygen gas the

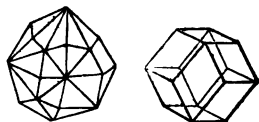


Fig. 23.

Crystalline forms of the diamond.

diamond burns, combining with the oxygen to form carbon dioxide — a fact first proved by Lavoisier in 1755. Two of the crystalline forms of the diamond are shown in the accompanying figure.

2. GRAPHITE.<sup>1</sup>—This useful variety of carbon is found crystallised in a form quite different from that of the diamond. It occurs in the oldest rocks of Cumberland (Borrowdale), Germany (Griesbach), Ceylon, Siberia, Australia (Moreton Bay), and America (State of New York and Massachusetts). Some geologists are inclined to regard graphite—or *plumbago*, as it is sometimes called—as transformed coal.<sup>2</sup> Graphite sometimes occurs destitute of crystalline form, or *amorphous*.<sup>3</sup> Native graphite in its purest form consists of pure carbon; less pure forms contain sometimes as much as five per cent. of iron and other impurities. It is an opaque solid, with a steel-grey lustre, having a specific gravity of 1.209. Amorphous graphite is much used for writing-pencils, its metallic appearance having led to the erroneous designation of *black-lead*. It was formerly thought necessary that the graphite for pencils should be cut out of a block of the native mineral, but it is now found that finely-powdered plumbago, when submitted to enormous pressure in the hydraulic press, forms a

<sup>1</sup> G. *grapho*, I write. Applied because this variety of carbon is used for pencil making.

<sup>2</sup> See, for instance, Lyell's "Elements of Geology," p. 567.

<sup>3</sup> G. *a*, without; *morphe*, a shape.

coherent cake, which can be sawn up into slabs, and then into the long strips necessary for pencils. In this manner the smallest fragments can be utilised. When treated with a powerful oxidising mixture—such as potassium chlorate and nitric or sulphuric acid—graphite forms a soluble compound containing carbon, hydrogen, and oxygen, and termed by Sir Benjamin Brodie *graphitic acid*. This reaction is made use of for the purification of impure graphite, since the acid on ignition leaves pure graphite in a state of fine division.

Graphite may be produced artificially by the intense ignition of the various forms of amorphous carbon (to be considered immediately) in the electric arc; also in the crystalline form by dissolving charcoal in molten cast iron, when it separates out on cooling in black scale-like crystals. Amorphous graphite also separates under certain circumstances from the mother-liquors of the soda manufacture, a branch of chemical industry which will be treated of in a subsequent chapter. Plumbago dust is used for diminishing the friction of the various parts of machinery, for polishing the surfaces of iron to be protected from the air, and, when mixed with clay, for making crucibles.

3. AMORPHOUS CARBON.—This variety of carbon is familiar under several well-known forms—such as coke, wood and animal charcoals, and lampblack.

*Coke* is the dull black porous mass left when coal is heated in a close vessel. Coke consists chiefly of carbon, but leaves a certain quantity of ash when burnt. It is used for fuel, and in certain districts for iron smelting. A very dense form of coke known as “glance-coal” is found in the upper portions of the retorts used for distilling coal for coal-gas, and is used for making the negative element of Bunsen’s battery, and also for the poles of the electric lamp.

*Charcoal* is obtained by heating organic substances in closed vessels so as to prevent access of oxygen, and

is either animal or vegetable, according to the nature of the substance employed.

Wood-charcoal is obtained by heating wood in iron retorts or by burning billets of wood stacked in conical heaps and covered over with turf, air-holes being left open at the bottom of the heap. The former plan is chiefly carried out in this country, where large quantities of wood are distilled for the preparation of the so-called "wood-vinegar." The latter plan is carried out in the Harz Mountains of Germany, and in other continental countries where wood is abundant. Wood is a chemical compound of carbon, hydrogen, and oxygen: when heated the hydrogen and oxygen are given off, and the carbon remains as a black porous solid, which retains the form, and even the structure, of the original wood.

Animal charcoal, or "bone-black," is obtained by the carbonisation of bones in closed iron vessels. This variety of charcoal is generally seen in the form of coarse grains.

Wood-charcoal possesses in a high degree the property of absorbing and condensing certain gases in its pores, and upon this property depends its use as a disinfectant for purifying infected atmospheres. Animal charcoal, on the other hand, possesses the power of abstracting certain organic matters from aqueous solutions, and is hence largely used for decolourising syrups in the process of sugar refining.

For this same reason animal charcoal should always be employed to filter impure water used for drinking purposes, since the organic contaminations are thereby removed. Animal charcoal is not pure carbon, but contains a large quantity of earthy matter, chiefly consisting of tricalcium diphosphate, or "bone earth" [ $\text{Ca}_3(\text{PO}_4)_2$ ].

*Lampblack* is carbon in a very fine state of division, and is chiefly used as a pigment. It is prepared by burning pitch, resin, &c., with a limited supply of air, and collecting the lampblack in suitable chambers.

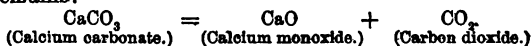
## 1. COMPOUNDS OF CARBON WITH OXYGEN.

## 34. CARBON DIOXIDE.

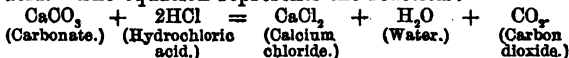
Symbol,  $\text{CO}_2$ . Molecular weight, 44.

**Occurrence.**—This gas exists, as we have already mentioned, in small quantities in the atmosphere. It issues also from fissures in the ground in certain volcanic districts, and is evolved from active volcanoes in enormous quantities. All natural waters contain carbon dioxide in solution.

**Preparation.**—When carbon or any compound of carbon is burnt in the air or in oxygen, carbon dioxide is produced. This gas is also given off when certain carbonates are strongly heated. Thus, in the case of chalk (calcium carbonate), calcium oxide or quicklime remains:—



For ordinary purposes the gas is prepared by acting on a carbonate (usually calcium carbonate, as chalk or marble) with some stronger acid, such as hydrochloric acid. The equation represents the reaction:—



The flask employed for preparing hydrogen (see p. 35)

may be used for the preparation of carbon dioxide. A very convenient arrangement for obtaining a constant supply of the gas is shown in the annexed figure; and by substituting zinc for marble this same arrangement can be used for obtaining a constant supply of hydrogen.

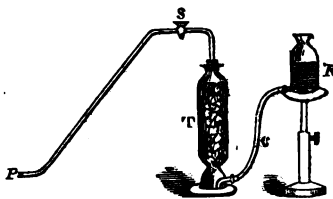


Fig. 24.  
Carbon dioxide: constant supply apparatus.

T is a bottle of the form shown in the figure, containing fragments of marble, and fitted with a cork and bent tube having a stopcock at S. The bottle R, having an opening near the bottom, contains dilute hydrochloric acid. The openings at the bottom of R and of T are plugged with perforated corks, through which pass short pieces of glass tubing: the two short glass tubes are connected by a piece of flexible india-rubber tubing (C). To use the apparatus the bottle of acid must be raised on a stand above the level of the marble in T. On opening the stopcock the acid descends through C, and rising up through the marble causes a disengagement of gas, which passes out through the bent tube P and may be collected at the pneumatic trough or by downward displacement. When the stopcock S is closed the pressure of the gas drives the acid back into R and so arrests the disengagement of gas.

**Properties.**—Carbon dioxide is at ordinary temperatures a colourless, transparent, and inodorous gas, having a slightly acid taste. It is not combustible, neither does it support the combustion of a lighted taper; but certain metals having a strong affinity for oxygen—such as potassium and magnesium—burn in the gas, combining with the oxygen and liberating the carbon. At the freezing point of water, under a pressure of 36 atmospheres, carbon dioxide passes into a colourless liquid; and this liquid, when allowed to evaporate in any quantity, absorbs so much heat that a portion solidifies to a snow-like mass. The liquefaction of the gas may be effected at the ordinary atmospheric pressure when it is cooled down to  $-87^{\circ}$ , and at the same temperature, under a pressure of 4 atmospheres, the liquid becomes a transparent ice-like solid. Solid carbon dioxide may be gently handled in spite of its very low temperature, because it is always giving off gas which prevents actual contact with the skin. If pressed between the fingers, however, it produces a blister similar to that caused by a burn. Liquid carbon dioxide boils under ordinary



atmospheric pressure at  $-78.2^{\circ}$ , and when heated the liquid expands more than the gas for equal increments of temperature, being in this respect quite exceptional. By means of the cold produced by a mixture of solid carbon dioxide and ether ( $-81^{\circ}$ ) it is possible to freeze water in a red-hot crucible, for the cushion of gas surrounding the ethereal liquid is a very bad conductor of heat and prevents actual contact with the red-hot metal.<sup>1</sup> A small capsule of water plunged into the centre of the liquid instantly freezes.

Carbon dioxide gas is not respirable—animals immersed in it soon die. Even when largely diluted with air, the gas is deleterious, acting as a narcotic poison.

The density of carbon dioxide referred to hydrogen is  $12 \div \frac{1}{2} = 22$ . One litre weighs 1.97 grammes. Owing to the great weight of the gas, it may be poured from one vessel into another like water, and for the same reason it often accumulates at the bottom of wells, limestone caverns, &c.

Carbon dioxide, according to the experiments of Regnault and Magnus, expands rather more than atmospheric air for an equal increase of temperature, thus departing slightly from the law of Charles, previously considered (p. 69).

Since the molecule of carbon dioxide contains two atoms of oxygen, it follows that a given volume of the gas contains its own volume of oxygen. This may be proved by collecting a certain quantity of the gas over mercury, passing up a fragment of charcoal, and then noting the volume. The charcoal is then heated till it enters into combustion, after which the gas is allowed to cool, when its volume will be found unaltered, although completely converted into carbon dioxide.

Water dissolves carbon dioxide, forming a solution which possesses slightly acid properties. At ordinary

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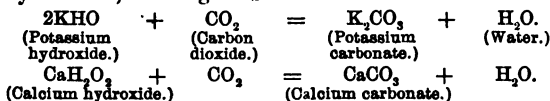
<sup>1</sup> This is the "spheroidal state" of Leidenfrost, for further details of which the student is referred to some work on Physics.

temperatures water dissolves about its own volume of the gas; at  $0^{\circ}$  one volume of water dissolves 1.797 volumes of gas. On boiling an aqueous solution, the whole of the gas escapes. The weight of carbon dioxide absorbed by water increases with the pressure to which the gas is submitted (in presence of the water). When the pressure is relieved, the excess of gas escapes with effervescence, as we see when the cork is drawn from a bottle of soda-water, champagne, or other liquid saturated with carbon dioxide.

The aqueous solution of carbon dioxide is supposed to contain an acid—the so-called *carbonic acid* ( $\text{H}_2\text{CO}_3$ )—since it is faintly sour to the taste, reddens blue litmus, and forms a series of compounds termed *carbonates* when made to act on certain metallic oxides and hydroxides. Carbon dioxide is for this reason sometimes called *carbonic anhydride*. The acid has, however, not yet been isolated, since it is so very unstable that it splits up into water and the anhydride with the greatest readiness:—



Carbon dioxide is rapidly absorbed by many metallic hydroxides, forming carbonates:—



Owing to this property, potassium hydroxide is always employed to absorb carbon dioxide in cases where the gas is to be weighed. In estimating the quantity present in the atmosphere, for instance, a series of U-tubes are filled with sticks of potassium hydroxide and weighed; a known quantity of dry air is then passed through them; and the increase in weight gives the quantity of carbon dioxide in that quantity of air.

The best test for the presence of carbon dioxide is lime-water, which is a clear solution of calcium

hydroxide. In accordance with the above equation, the gas, when passed through lime-water, produces calcium carbonate, which, being insoluble, causes a white turbidity.

*The Chemistry of Respiration.*—It has already been mentioned that oxygen is essential for respiration (p. 48). With a knowledge of the law of diffusion of gases and of the composition and properties of carbon dioxide, the student may now resume this subject.

In the lungs of animals the blood is exposed in fine thin-walled vessels, called *capillaries*,<sup>1</sup> to the action of atmospheric air. The air thus taken into the lungs loses a certain amount of oxygen and gains a certain quantity of carbon dioxide and water-vapour. This vitiated<sup>2</sup> air, when expired from the lungs, contains from three to six per cent. of carbon dioxide, and will not support the combustion of a lighted taper. The actual weight of carbon dioxide expired averages about 77 grammes per hour during a working day, and 44·5 grammes per hour during a day rest. The water excreted<sup>3</sup> is about 91 grammes per hour during a day of work, and about 29 grammes during a day of rest. The amount of oxygen absorbed is 19·5 grammes per hour during a day of rest, and about 24·5 grammes during a working day. By night more oxygen is absorbed, and less carbon dioxide is excreted than during the day. The oxygen absorbed by the blood is distributed to all parts of the body by the circulatory system, and serves to oxidise the waste products, this oxidation giving rise to the high temperature of the animal body. The results of this oxidation are carbon dioxide and water, which are brought into the lungs by the blood, and there exposed to the inspired air, as

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<sup>1</sup> *L. capillus*, a hair. A technical expression applied to very fine tubes.

<sup>2</sup> *L. vitio*, to corrupt.

<sup>3</sup> *L. excretum*, refuse.

already described. The aëration of the blood effects the removal of carbon dioxide and water, while oxygen is absorbed; this interchange of gases being effected through the membranous walls of the capillaries by a process of diffusion. The blood thus purified is again ready to perform its oxidising functions, and is once more circulated through the system.

The carbon dioxide given off during respiration may be shown by blowing through lime-water, which soon becomes milky; while the water exhaled may be shown by blowing through a long cold glass tube, the inside of which immediately becomes covered with moisture.

Now, as animals are continually consuming oxygen and pouring out carbon dioxide into the atmosphere, and as this gas is, moreover, being given out by all burning bodies containing carbon, as well as from fissures in the earth and from active volcanoes, the student may naturally inquire how it is that the atmosphere has not undergone deterioration in the course of time; how it is that the oxygen has not been gradually replaced by carbon dioxide.

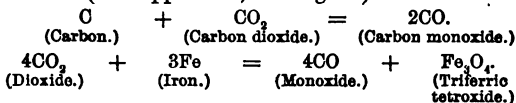
It has been found, in reply to this question, that *plants* inhale carbon dioxide, and under the influence of sunlight decompose this gas into its constituent elements, retaining the carbon to form their own tissues, and liberating the oxygen in the free state. Thus do animals and plants mutually supply each other with the gases necessary for their existence, and the carbon dioxide excreted by animals is decomposed into carbon and oxygen by plants under the influence of sunlight.

When plants are imbedded in the earth they undergo gradual decomposition; most of their volatile portions escape; and the carbon which entered into their composition is left behind, in combination with small quantities of hydrogen and nitrogen, as *coal*. To the consideration of this important substance we shall, however, return when treating of Organic Chemistry.

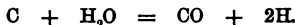
### 35. CARBON MONOXIDE.

Symbol, CO. Molecular weight, 28.

**Preparation.**—This oxide of carbon is obtained by passing carbon dioxide over iron or charcoal heated to redness. (For apparatus, see Fig. 3.)

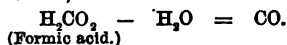
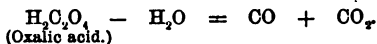


It is also produced with hydrogen when steam is passed over red-hot carbon :—



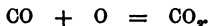
The mixture of gases thus obtained is known as "water-gas."

Carbon monoxide is also prepared by heating certain organic compounds—such as oxalic and formic acids—with sulphuric acid. The reaction depends upon the withdrawal of the elements of water by the sulphuric acid :—



When sulphuric acid is heated with a complex organic compound termed potassium ferrocyanide ( $\text{K}_4\text{FeC}_6\text{N}_6$ ) carbon monoxide is also produced.

**Properties.**—Carbon monoxide is a colourless and transparent gas possessing hardly any odour. It has never been liquefied. Its density referred to air is 0.968; referred to hydrogen it is 14; so that one litre weighs 1.25 grms. The gas does not support combustion, but it burns in the air with a beautiful blue flame, producing carbon dioxide :—



When mixed with oxygen carbon monoxide explodes on the application of a burning body, 2 vols. of the gas combining with 1 vol. of oxygen to produce 2 vols. of

$\text{CO}_2$ . Now, as 2 vols. of  $\text{CO}_2$  contain 2 vols. of O (p. 118), it follows that 1 vol. of O has been derived from the CO, because only one 1 vol. of O is used up in the reaction: hence CO contains half its volume of O. Carbon monoxide is extremely poisonous, and does not produce a turbidity in lime-water. The danger of burning charcoal in close rooms arises from the poisonous nature of the gas. The blue flame seen on the top of a clear fire is due to the combustion of carbon monoxide. This gas combines directly with chlorine under the influence of sunlight, forming a transparent suffocating gas, termed carbon oxydichloride, or phosgene<sup>1</sup> gas ( $\text{COCl}_2$ ). Carbon monoxide is sometimes termed *carbonic oxide*.

## 2. COMPOUNDS OF CARBON WITH HYDROGEN.

Carbon forms an immense number of compounds with hydrogen. These compounds, termed *hydrocarbons*, will be treated of in the volume on Organic Chemistry.

## 3. COMPOUND OF CARBON WITH NITROGEN.

Carbon forms a compound with nitrogen—Cyanogen ( $\text{CN}$ )<sub>2</sub>—which will be considered among organic compounds.

## 4. COMPOUNDS OF CARBON WITH THE HALOGENS.

As these substances are obtained from organic compounds, their preparation will be described under Organic Chemistry. The student may here make himself acquainted with their names and formulæ so far as they are known.

### Chlorides.

Dicarbon dichloride .....	$\text{C}_2\text{Cl}_2$
Dicarbon tetrachloride .....	$\text{C}_2\text{Cl}_4$
Dicarbon hexachloride .....	$\text{C}_2\text{Cl}_6$
Carbon tetrachloride .....	$\text{CCl}_4$

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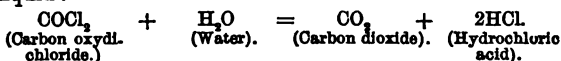
<sup>1</sup> G. *phōs*, light; *gēnnāō*, I produce. Applied because this substance is produced under the influence of light.

## Bromides.

Dicarbon tetrabromide.....	$C_2Br_4$ .
Dicarbon hexabromide.....	$C_2Br_6$ .
Carbon tetrabromide.....	$CBr_4$ .

No compound of carbon with iodine has hitherto been obtained. By acting on silver fluoride ( $AgF$ ) with chlorine in vessels of graphite a fluoride of carbon has been obtained by Mr. Gore.

Compounds of carbon with chlorine and hydrogen, bromine and hydrogen, and with iodine and hydrogen exist, but these will also be considered as organic compounds. The compound of carbon with chlorine and oxygen, carbon oxydichloride ( $COCl_2$ ), or phosgene gas, has just been mentioned. This substance is a colourless gas having a most pungent and suffocating odour. By a mixture of ice and salt it may be liquefied, and then forms a limpid<sup>1</sup> liquid which sinks in water and gradually undergoes decomposition in presence of this liquid:—



Liquid phosgene boils between  $8^\circ$  and  $9^\circ$ ; its specific gravity is about 1.4. The density of the gas is 49.5 ( $COCl_2 = \frac{12 + 16 + (35.5 \times 2)}{2} = 49.5$ ).

36. SILICON.<sup>2</sup>

Symbol, Si. Atomic weight, 28.

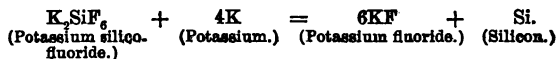
**Occurrence.**—After oxygen, which forms about 46 per cent. by weight of the earth's solid crust, silicon is the most abundant of the elements, forming about 29½ per cent. of the earth's crust. This element never occurs in the free state, but always in combination with oxygen as a dioxide, or in combination with oxygen and metals forming a very extensive class of minerals termed *silicates*.

<sup>1</sup> L. *limpidus*, transparent.

<sup>2</sup> The name of the element is from a word of Latin origin—*silex*—signifying a flint-stone.

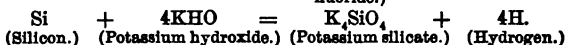
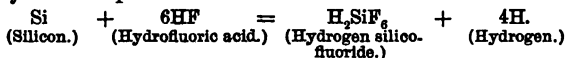
**Preparation.**—Silicon, like carbon, exists in three modifications:—

1. **AMORPHOUS SILICON.**—This form of the element is prepared by heating a compound of potassium, fluorine, and silicon, with metallic potassium in a glass or iron tube:—

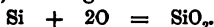


It may also be obtained by passing the vapour of silicon tetrachloride over potassium or sodium heated in a glass tube, and likewise by passing an electric current through a fused mixture of potassium silico-fluoride and potassium fluoride.

Amorphous silicon is a brown powder, insoluble in water, but soluble in hydrofluoric acid and in a warm solution of potassium hydroxide. The compounds formed in these two cases will be best seen from the symbolic representation of the reactions:—



When heated in air or oxygen amorphous silicon burns brilliantly, forming the dioxide:—



When heated to the melting point of cast-iron in an atmosphere that exerts no action upon it, it fuses.

2. **GRAPHITOIDAL<sup>1</sup> SILICON.**—This modification may be obtained by strongly heating amorphous silicon, or by fusing amorphous silicon with metallic aluminium, and then treating the fused mass with hydrochloric and hydrofluoric acids alternately, the aluminium and excess of amorphous silicon being thereby removed, while graphitoid silicon is left in the form of crystalline scales, having a specific gravity of 2.49.

<sup>1</sup> That is, a form of silicon analogous to the graphite form of carbon.



Silicon in this form may be heated to whiteness in oxygen without burning, but it burns when heated to redness in chlorine, forming silicon tetrachloride. Solution of potassium hydroxide acts but slowly upon graphitoïdal silicon, while hydrofluoric acid is without action unless mixed with nitric acid.

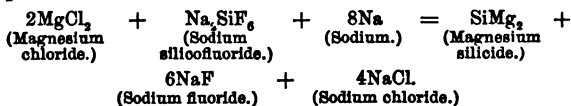
3. **DIAMOND SILICON.**—This form of silicon, corresponding to the diamond, is best prepared by adding zinc to the mixture used for obtaining amorphous silicon, and heating to redness in an earthen crucible. The mass is then boiled with hydrochloric and nitric acids respectively, the zinc being by this treatment dissolved away, while the silicon remains in the form of dark iron-grey needle-shaped crystals, which are hard enough to cut glass. Silicon was first obtained (in the amorphous form) by Berzelius in 1823.

#### 1. COMPOUND OF SILICON WITH HYDROGEN.

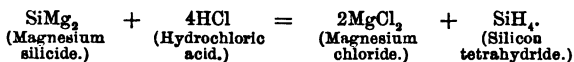
### 37. SILICON TETRAHYDRIDE (Silicated Hydrogen).

Symbol,  $\text{SiH}_4$ . Molecular weight, 32.

**Preparation and Properties.**—This gas is obtained, mixed with hydrogen, by passing an electric current through dilute sulphuric acid, using a plate of aluminium containing silicon for the negative pole. The nascent hydrogen here combines with the silicon. Another method frequently employed is the following:—Magnesium chloride is fused with sodium silicofluoride and metallic sodium, whereby magnesium silicide is produced, thus:—

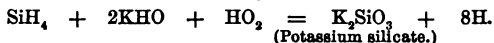


Magnesium silicide, when treated with hydrochloric acid, yields silicon tetrahydride:—



Another method of obtaining this gas (in a pure state) has been recently discovered, but the process involves the use of an organic compound, and must therefore be deferred for the present.

Siliciuretted hydrogen is a colourless gas which takes fire spontaneously on coming into contact with the air, forming water and silicon dioxide. It is decomposed by heat alone, yielding amorphous silicon and hydrogen. Potassium hydroxide also decomposes the gas, forming potassium silicate and free hydrogen :—



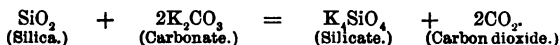
## 2. OXIDE AND ACID OF SILICON.

### 38. SILICON DIOXIDE (Silica).

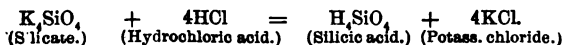
Symbol,  $\text{SiO}_2$ . Molecular weight, 60.

**Occurrence.**—This oxide occurs abundantly in nature in the pure state in many minerals. It is found crystallised as quartz or rock-crystal, and amorphous as flint, agate, chalcedony, jasper, opal, sandstone, &c. In combination with metallic oxides silica enters into the composition of most of the minerals forming the earth's crust.

**Preparation.**—To obtain this compound in the pure state finely-powdered flint or sand is fused with potassium carbonate :—



When the potassium silicate is dissolved in water and acidulated with hydrochloric acid, silicic acid is liberated and remains partly in solution, but the greater portion comes down as a gelatinous mass :—



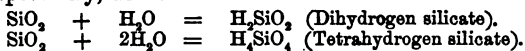
The gelatinous acid is filtered off, washed, and ignited, when it splits up into water and silicon dioxide:—



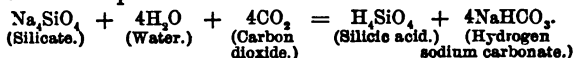
**Properties.**—Silica as obtained by the above process is a light white powder possessing neither taste nor smell. It requires a very high temperature for its fusion, and is not attacked by any acid, excepting hydrofluoric. The specific gravity of this amorphous silica is from 1.9 to 2.3, while the native crystals of quartz have a specific gravity varying from 2.5 to 2.8 and are hard enough to scratch glass. Silica, in the amorphous condition, is dissolved by potassium and sodium hydroxide, with the formation of potassium or sodium silicate. We have seen also that silica is capable of expelling carbonic anhydride when fused with an alkaline carbonate. These and other considerations justify us in considering silica as the anhydride of an acid, and it is in consequence frequently spoken of as *silicic anhydride*.

### 39. SILICIC ACID.

This acid may be regarded as a compound of silicic anhydride with water, just as nitric acid may be considered as a compound of nitric anhydride with water (see p. 60). There are probably two well-defined silicic acids known, formed by the union of a molecule of the anhydride with *one* and *two* molecules of water respectively, thus:—

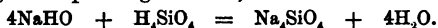


The last of these acids is formed when hydrochloric acid is added to a solution of a soluble silicate, as in the second stage of the preparation of silicon dioxide (p. 127). A similar decomposition is effected by carbon dioxide in presence of water:—



A decomposition analogous to the above is constantly going on in nature, causing the disintegration<sup>1</sup> of rocks composed of metallic silicates.

Silicic acid is a jelly-like substance soluble to a certain extent in water. The aqueous solution may be concentrated till it contains 14 per cent. of the acid, which is, however, deposited on standing as a clear jelly. Silicic acid dissolves in solutions of potassium and sodium hydroxide, forming corresponding silicates, thus:—



It is slightly soluble also in ammonia and in many acids.

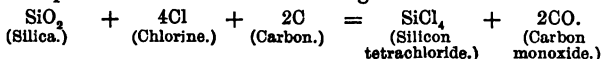
The dihydric silicic acid is obtained as a glassy transparent substance by evaporating the aqueous solution of the tetrahydric acid *in vacuo* over sulphuric acid (to absorb the water vapour) at the ordinary temperature of the air.

### 3. COMPOUNDS OF SILICON WITH THE HALOGENS.

#### 40. SILICON TETRACHLORIDE.

Symbol,  $\text{SiCl}_4$ . Molecular weight, 170.

**Preparation and Properties.**—This compound may be obtained by burning silicon in chlorine, or more conveniently by passing dry chlorine over a mixture of finely-divided silica and charcoal dust heated to redness in a porcelain tube. The following reaction occurs:—



The general disposition of the apparatus may be gathered from Fig. 3. The delivery tube is replaced by a condensing arrangement containing a freezing mixture, the iron tube by a porcelain tube filled with the mixture of silica and charcoal (in the form of pellets), and the flask of boiling water by a flask containing the mixture for generating chlorine.

<sup>1</sup> Meaning the gradual breaking up into parts. (L. *dis*, asunder; *integer*, whole.)

Silicon tetrachloride is a transparent and colourless liquid, the vapour of which possesses a suffocating odour. Its specific gravity at  $0^\circ$  is 1.523; its boiling point is  $50^\circ$ . The density of the vapour is 5.9 referred to air, and  $\frac{28 + (3.5 \cdot 5 \cdot 4)}{2} = 85$  referred to hydrogen; one litre weighs consequently 7.6 grammes.

Water quickly decomposes silicon tetrachloride into hydrochloric and silicic acids.

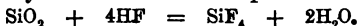
The corresponding compounds of silicon with bromine and iodine have been obtained by somewhat similar processes. The names and formulæ of these, together with some other compounds of silicon, are given below, space not permitting us to enter fully into their preparation and properties:—

			Boiling point.	Melting point.
Silicon tetrabromide	... $\text{SiBr}_4$	...	$153.4^\circ$	...
Silicon tetriodide	... $\text{SiI}_4$	...	...	$120.5^\circ$
Disilicon hexiodide	... $\text{Si}_2\text{I}_6$	...	...	$250^\circ$
Silicon hydrotrichloride	... $\text{SiHCl}_3$	...	$36^\circ$	...
Silicon hydrotriiodide	... $\text{SiHI}_3$	...	$220^\circ$	...

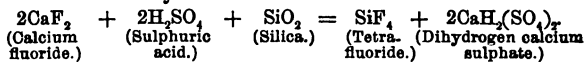
#### 41. SILICON TETRAFLUORIDE.

Symbol,  $\text{SiF}_4$ . Molecular weight, 104.

**Preparation and Properties.**—This compound is produced when hydrofluoric acid acts upon silica:—



It is most conveniently prepared by liberating hydrofluoric acid in presence of silica. This is effected by heating a mixture of fluor-spar, sand, and sulphuric acid in a flask provided with a delivery tube (see Fig. 25). The reaction is thus symbolised:—



Silicon tetrafluoride is a colourless gas which fumes in the air and possesses a highly pungent odour. It liquefies under great pressure and solidifies at  $-140^\circ$ . It is neither combustible nor a supporter of combustion.

It is owing to the strong affinity of fluorine for silicon that hydrofluoric acid etches glass. The reaction is similar to that which occurs in the preparation of fluoride of silicon by the action of hydrofluoric acid upon silica. In etching a design upon glass the object is first coated with wax and the design then engraved with a sharp point. The glass is then either exposed to the fumes of hydrofluoric acid given off from a mixture of fluor-spar and sulphuric acid heated together in a leaden trough, or else an aqueous solution of the acid is poured over it. The hydrofluoric acid attacks the unprotected portions of the glass, etching out the design and leaving the wax-coated portions unaltered.

**42. SILICOFLUORIC ACID** ( $\text{H}_2\text{SiF}_6$ ) is produced when silicon tetrafluoride is passed into water:—

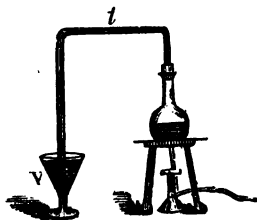
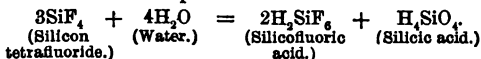


Fig. 25.  
Preparation of silicofluoric acid.

The flask F in the accompanying figure contains the mixture for generating silicon tetrafluoride. This gas passes down through the tube *t*, the end of which dips beneath the surface of some mercury in the vessel V, the remainder of the vessel being filled up with water.

The object of the mercury is to prevent the stopping up of the end of the tube by the gelatinous silicic acid which is deposited by each bubble as it comes in contact with the water. When the whole of the liquid has become gelatinous the silicic acid is removed by filtration, and the clear solution then contains the silicofluoric acid (sometimes called hydrofluosilicic acid).

A strong solution of this acid fumes in the air. The

hydrogen of silicofluoric acid, when replaced by metals, gives rise to a series of salts termed *silicofluorides*.

We may now pass on to the consideration of the element boron, which presents certain points of resemblance to the two elements just considered.

### 43. BORON.

Symbol, B. Atomic weight, 11.

**Occurrence.**—The element boron does not exist in nature in the free state, but occurs in combination with oxygen as boric acid and in combination with oxygen and sodium as native *borax*, or *tincal* ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ). The mineral *boracite* is a borate of magnesium containing magnesium chloride.

**Preparation and Properties.**—Boron is known under two forms :—

1. **AMORPHOUS BORON.**—This modification is best prepared by heating finely-powdered boron trioxide with metallic sodium to redness in an iron crucible.

Amorphous boron is a dark-brown powder possessing neither taste nor smell. It burns with a reddish flame when strongly heated in the air, and with intense brilliancy in oxygen, boron trioxide being produced in both these cases. Boron likewise burns when heated in nitrogen, forming a nitride (BN)—this being one of the few cases in which an element combines *directly* with nitrogen. Boron burns also when heated with chlorine, boron trichloride being the result of the combination.

2. **DIAMOND BORON** is obtained by submitting a mixture of amorphous boron and metallic aluminium to intense ignition for some hours. The fused metal dissolves the boron, which crystallises out on cooling.

This form of the element occurs in eight-sided crystals, varying from a slightly yellow tint to a deep red. Diamond boron possesses a density of 2.63, and some crystals are even as hard as the diamond. This form of boron is more inert in its chemical behaviour than the amorphous

modification. The crystals do not burn when strongly heated in oxygen.

Boron was first obtained (in the amorphous state) by Gay-Lussac and Thénard in 1808.

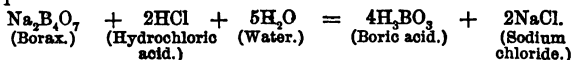
### 1. OXIDE AND ACID OF BORON.

**44. BORON TRIOXIDE.** ( $B_2O_3$ , Molecular weight, 70.)

**45. BORIC ACID.** ( $H_3BO_3$ , Molecular weight, 62.)

**Occurrence.**—Boric acid, mixed with large quantities of steam, issues from the earth in certain volcanic districts in Tuscany, from this source all the acid of commerce being derived. The sodium salt already referred to as *borax* is found chiefly in India and Thibet dissolved in the waters of salt lakes.

**Preparation.**—On a large scale in Tuscany, crude<sup>1</sup> boric acid is prepared by evaporating water which has taken up a certain quantity of the acid from the escaping steam jets (*suffioni*). The evaporation is effected by utilising the heat of the steam jets themselves, so that no fuel is required. Boric acid may be prepared in a purer state by adding sulphuric or hydrochloric acid to a hot aqueous solution of borax:—



The acid separates out on cooling in crystalline scales.

**Properties.**—Boric acid is a white crystalline inodorous substance possessing a slightly acid and bitter taste. It is slightly soluble in cold but more soluble in warm water. The crystals have a specific gravity of 1.48. The acid possesses the property of imparting a green tint to the flame of burning spirits of wine or other colourless flame. Boric acid, when its hydrogen is replaced by metals, gives rise to a series of salts termed *borates*, of which borax is the most important, being largely used as a *flux* (see foot-

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<sup>1</sup> L. *crudus*, raw. Applied in chemistry to impure substances.



note, p. 109) because at a red heat it possesses the property of dissolving metallic oxides.

Boric acid, when strongly heated, loses water and leaves boron trioxide :—



This oxide may therefore be termed *boric anhydride*. It is a brittle glassy substance which has a slightly bitter taste and a specific gravity of 1.83. It is likewise formed when amorphous boron burns in oxygen.

The other compounds of boron are not of sufficient importance to claim the student's attention at this stage of his studies. Their names and formulæ are given below :—

Boron nitride .....	BN.
Boron trichloride .....	$\text{BCl}_3$ .
Boron tribromide .....	$\text{BBr}_3$ .
Boron trifluoride.....	$\text{BF}_3$ .
Hydrofluoboric acid .....	$\text{HBF}_4$ .

**Summary.**—1. The elements carbon and silicon are closely related to each other in their properties. Boron presents certain points of resemblance to the elements of the carbon group.

2. Carbon and silicon are capable of existing in three forms: (i) the diamond, or *adamantine*<sup>1</sup> form; (ii) the graphitoid form; (iii) the amorphous form.

3. Boron is known only in the amorphous and adamantine modifications.

4. Amorphous carbon is known under the various forms of coke, wood-charcoal, animal-charcoal or bone-black, soot, and lampblack.

5. Carbon forms two oxides, a monoxide, and a dioxide. Silicon forms only a dioxide.

6. Carbon dioxide is prepared by acting on chalk or marble (calcium carbonate) with hydrochloric acid. Carbon monoxide is formed when the dioxide is passed over heated carbon or iron.

7. Animals require oxygen for respiration, and give out carbon dioxide. Plants require carbon dioxide, which they decompose under the influence of sunlight, retaining the carbon and giving out the oxygen.

8. Carbon forms compounds with chlorine, bromine, and perhaps with fluorine. Silicon likewise forms compounds with chlorine and

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<sup>1</sup> G. a, not; *damaõ*, I break. Applied to very hard stones, such as the diamond.

bromine. It unites also with iodine, and possesses a strong affinity for fluorine.

9. Many silicates are decomposed by hydrofluoric acid. Hence the use of this acid for etching glass.

10. Silicon in combination with hydrogen and oxygen forms silicic acid. Boron, in combination with these elements, forms boric acid. Boric acid when strongly heated leaves boron trioxide, the only known oxide of boron.

11. Amorphous boron combines directly with nitrogen, also with oxygen and certain of the halogens.

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## CHAPTER VII.

### THE SULPHUR GROUP.

THE three elements sulphur, selenium, and tellurium form a natural group, which in its chemical relationships presents many points of resemblance to oxygen. Oxygen having already been considered (Chapter II.), we now pass on to the chemistry of the above-named elements, forming what is called the sulphur group.

#### 46. SULPHUR.<sup>1</sup>

Symbol, S. Atomic weight, 32.

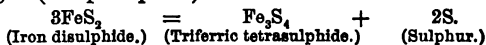
**Occurrence.**—This element is found in the free state in volcanic regions in the crystalline form, its chief districts being in Sicily, Iceland, and Mexico. The crystals are sometimes transparent and reddish-brown, sometimes opaque and lemon-yellow in colour. Sulphur occurs also in combination with metals as sulphides, and in combination with metals and oxygen, forming sulphates. Of sulphides the most important are *iron-pyrites* (iron disulphide,  $\text{FeS}_2$ ), *copper-pyrites* ( $\text{Fe}_2\text{S}_3\cdot\text{Cu}_2\text{S}$ ), *zinc blende* (zinc sulphide,  $\text{ZnS}$ ), *galena* (lead sulphide,  $\text{PbS}$ ), and *cinnabar* (mercury

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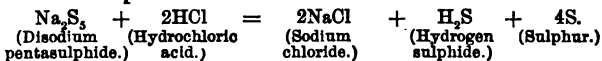
<sup>1</sup> L. *sal*, salt; G. *pur*, fire. Applied because of its combustible nature.

sulphide, HgS). Sulphur exists also in small quantities in certain constituents of animal and vegetable organisms.

**Preparation.**—Sulphur is extracted from its ores for commercial purposes by distilling the mineral (either native sulphur or iron-pyrites) in earthen pots connected with condensers of a similar material. The decomposition of iron-pyrites by heat will be seen to be analogous to the decomposition of manganese dioxide in preparing oxygen (compare p. 39):—



**Properties.**—At ordinary temperatures sulphur is a yellow brittle solid, perfectly tasteless, and possessing hardly any odour. It is quite insoluble in water, so that the custom of putting a stick of sulphur into the water given to dogs is highly absurd. Sulphur is seen commonly under the three following forms:—(1) "roll-sulphur," or brimstone, obtained by melting sulphur and casting it into sticks; (2) "flowers of sulphur," obtained by rapidly cooling the vapour of sulphur; (3) "milk of sulphur," a white powder thrown down when hydrochloric or any other mineral acid<sup>1</sup> is added to a solution of an alkaline sulphide:—



Sulphur behaves in a most singular manner when heated. At 114.5° it melts and forms a thin amber-coloured liquid; on further heating it becomes viscous and darker in colour, and at a temperature of 235° is so thick that the vessel containing it can be inverted without loss of the contents. Above this temperature it again becomes fluid, but not so fluid as when first melted. At 440° sulphur boils, and gives off an orange-coloured vapour. When allowed to cool down from its boiling

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<sup>1</sup> The three acids, hydrochloric, nitric, and sulphuric, are frequently spoken of as the *mineral acids*.

point it goes through the changes just described in inverse order.

Sulphur is remarkable for the many modifications in which it is known to exist, the three most important forms being as follows :—

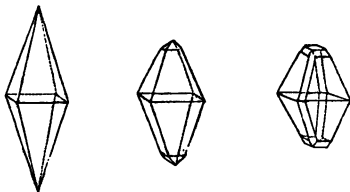


Fig. 26.

Crystals of octohedral sulphur.

1. OCTOHEDRAL<sup>1</sup> SULPHUR; so called on account of the form of its crystals (Fig. 26). This is the form in which native sulphur occurs, and is also the form assumed by sulphur when

allowed to crystallise from its solution in carbon disulphide, a liquid in which this variety of sulphur is readily soluble.<sup>2</sup> The specific gravity of octohedral sulphur is 2.05.

2. PRISMATIC SULPHUR; so called because the crystals have the form of lengthened prisms.<sup>3</sup> This form is obtained when melted sulphur is allowed to cool gradually; also by heating the octohedral variety for some time to a temperature of 110°. Prismatic sulphur, like the octohedral form, is soluble in carbon disulphide. The crystals have a specific gravity of 1.98, and by long keeping become converted into the octohedral variety.

3. PLASTIC SULPHUR is produced when sulphur, heated to a temperature of about 300°, is cooled suddenly by being poured into water. This variety of sulphur presents

<sup>1</sup> G. *oktō*, eight; *hēdra*, a seat.

<sup>2</sup> The preparation and properties of this compound will be considered in a future portion of this chapter. Under certain conditions this form of sulphur can also be obtained by the slow cooling of a fused mass of the substance.

<sup>3</sup> "A prism is a solid figure contained by plane figures, of which two that are opposite are equal, similar, and parallel to one another; and the others parallelograms."

the appearance of a yellowish-brown substance, capable of being drawn out into thin threads. Plastic sulphur passes in the course of a few hours into the octohedral form: when heated to  $100^{\circ}$  the change takes place instantly with elevation of temperature. The specific gravity of this modification is 1.95, and it is insoluble in carbon disulphide.

"Milk of sulphur" has been already alluded to. This form is soluble in carbon disulphide, and passes by keeping into the octohedral modification. "Flowers of sulphur" are allied to this form, while "roll-sulphur," when first cast, is in the "prismatic" modification.

Sulphur is exceedingly inflammable, burning in the air with a lambent blue flame, and giving off a most pungent odour, due to the formation of sulphur dioxide. Sulphur combines directly with most of the metals when heated with them: copper, zinc, iron, and silver burn in the vapour of sulphur with great brilliancy.

The vapour density of sulphur, taken at a temperature of  $1000^{\circ}$  and referred to hydrogen, is 32, in accordance with the law so frequently referred to (p. 61). At this temperature of  $1000^{\circ}$ , then, two volumes of sulphur vapour contain two atomic weights—the molecule is, in fact, *diatomic*. Near its boiling point ( $500^{\circ}$ ), however, the vapour density is 96 referred to hydrogen, so that the molecule (2 volumes) weighs  $96 \times 2 = 192$  compared with the molecule of hydrogen, and contains in consequence  $\frac{192}{32} = 6$  atomic weights—in other words, sulphur is at this temperature a *hexatomic* molecule. (Compare table on p. 13.)

## 1. COMPOUND OF SULPHUR WITH HYDROGEN.

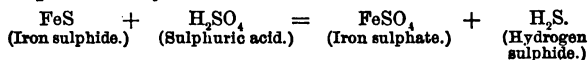
### 47. HYDROGEN SULPHIDE

(Sulphuretted Hydrogen or Sulphydric Acid).

(Symbol,  $H_2S$ . Molecular weight, 34.)

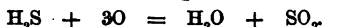
**Occurrence.**—This gas is found in certain mineral waters—such as those at Harrogate—and is contained also in the gases evolved from volcanoes.

**Preparation.**—Sulphur and hydrogen combine directly, when heated together, to form this compound; it is usually prepared, however, by acting on iron sulphide with dilute sulphuric or hydrochloric acids:—



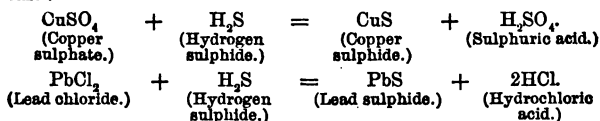
The form of apparatus is shown in Fig. 7.

**Properties.**—Hydrogen sulphide is a colourless and transparent gas possessing an intolerably fœtid odour, usually compared to that of rotten eggs. It is not a supporter of combustion, and acts as a poison when inhaled. When kindled in the air it burns with a bluish flame, giving off water and sulphur dioxide:—



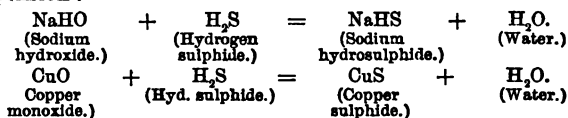
Hydrogen sulphide is dissolved in considerable quantities by cold water, so that warm water should be used in the pneumatic trough when collecting the gas. The aqueous solution of the gas possesses the peculiar odour of the gas itself. Under a pressure of about 17 atmospheres at the ordinary temperature of the air, or when cooled down to  $-74^\circ$  under the ordinary atmospheric pressure, this gas condenses to a colourless liquid, which at a temperature of  $-85.5^\circ$  becomes a solid transparent mass. The density of the gas referred to hydrogen is 17.

Hydrogen sulphide precipitates many metals as sulphides when the gas is passed through a solution of the metallic salt:—

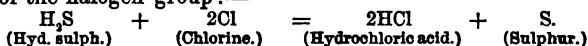


Owing to this property, hydrogen sulphide is a most valuable reagent for separating certain metals from one another, as we shall have occasion to see more fully hereafter. Most metals when heated in this gas combine with the sulphur and liberate the hydrogen. If a piece of tin

be heated in a measured quantity of the gas the residual hydrogen will be found to occupy the same volume as the original gas taken—showing that hydrogen sulphide contains its own volume of hydrogen. The gas is decomposed also at a red heat, sulphur being deposited and hydrogen liberated. Hydrogen sulphide can have its hydrogen partially or entirely replaced by metals, giving rise to a metallic sulphide or hydrosulphide. The replacement is effected when the gas is passed through water containing the metallic oxide or hydroxide in solution or in suspension :—



Hydrogen sulphide is decomposed also by the elements of the halogen group :—



## 2. OXIDES AND OXYGEN ACIDS OF SULPHUR.

The eight acids of sulphur have already been made use of to illustrate the law of multiple proportions (p. 9). In addition to these, two oxides are known; and as these give rise to acids when combined with water they are frequently spoken of as anhydrides. The student may now make himself acquainted with the names of these compounds :—

<i>Oxides.</i>	<i>Corresponding Acids.</i>
Sulphur dioxide, or Sulphurous anhydride ( $\text{SO}_2$ ).	Sulphurous acid ( $\text{H}_2\text{SO}_3$ ).
Sulphur trioxide, or Sulphuric anhydride ( $\text{SO}_3$ ).	
	Sulphuric acid ( $\text{H}_2\text{SO}_4$ ).
<i>Acids of which the Oxides are unknown.</i>	
Hydrosulphurous acid ( $\text{H}_2\text{SO}_2$ ).	Trithionic acid ( $\text{H}_2\text{S}_3\text{O}_6$ ).
Hyposulphurous acid ( $\text{H}_2\text{S}_2\text{O}_3$ ).	Tetrathionic acid ( $\text{H}_2\text{S}_4\text{O}_8$ ).
Dithionic <sup>1</sup> acid ( $\text{H}_2\text{S}_2\text{O}_6$ ).	Pentathionic acid ( $\text{H}_2\text{S}_5\text{O}_{10}$ ).

<sup>1</sup> G. *theion*, sulphur.

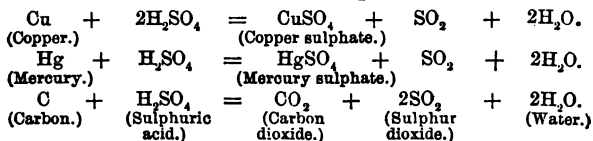
**48. SULPHUR DIOXIDE**

(Sulphurous Anhydride).

Symbol,  $\text{SO}_2$ . Molecular weight, 64.

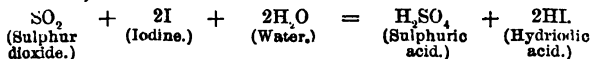
**Occurrence.**—This gas is evolved from volcanic craters and occurs in the spring waters of volcanic regions.

**Preparation.**—Sulphur dioxide is produced when sulphur burns in the air or in oxygen. It is generally prepared in the laboratory by heating strong sulphuric acid either with copper or mercury or with fragments of charcoal. A flask fitted with a cork and delivery-tube such as that used for preparing oxygen (Fig. 9) may be employed. The gas must be collected at the mercurial trough or by displacement, as it is largely absorbed by water. The reactions are thus expressed:—



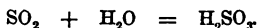
**Properties.**—Sulphur dioxide is a colourless gas of a most suffocating odour. It is neither combustible nor respirable, and a burning taper is extinguished on being plunged into the gas. When passed through a freezing mixture of ice and salt the gas liquefies, and when further cooled to  $-76^\circ$  the liquid is converted into a solid crystalline mass. The specific gravity of this gas is 32 referred to hydrogen or 2.25 referred to air.

Sulphur dioxide possesses powerful bleaching properties and likewise acts as a disinfectant. Wool, silk, and straw are bleached by being exposed in a moist state to the fumes of burning sulphur. Sulphur dioxide has a great tendency to take up oxygen, and thus acts as a powerful *reducing* agent. Its action upon iodine, for instance, is as follows:—

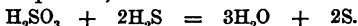




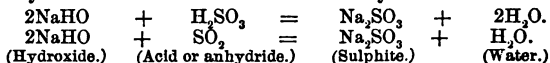
**49. SULPHUROUS ACID.**—Sulphur dioxide is largely absorbed by water, forming a solution which possesses the characteristic odour of the gas. When this aqueous solution is cooled down to  $0^{\circ}$  the true acid ( $\text{H}_2\text{SO}_3$ ) crystallises out. The acid may be therefore regarded as resulting from the union of a molecule of sulphur dioxide with a molecule of water :—



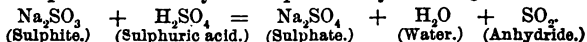
Sulphurous acid is not a very stable compound, since the aqueous solution when boiled gives off nearly the whole of its contained gas. By exposure to the air this acid absorbs oxygen and becomes gradually converted into sulphuric acid. Sulphurous acid and hydrogen sulphide react upon each other with the liberation of the sulphur from both compounds, thus :—



Sulphurous acid is the hydrogen salt of a series of salts termed *sulphites*, which may be formed by acting on metallic hydroxides with the acid or its anhydride :—



Sulphites are easily decomposable by a stronger acid :—



## 50. SULPHUR TRIOXIDE

(Sulphuric Anhydride).

Symbol,  $\text{SO}_3$ . Molecular weight, 80.

**Preparation and Properties.**—When sulphur dioxide mixed with oxygen is passed over finely-divided platinum heated to redness direct combination occurs, with the formation of this oxide :—



Sulphur trioxide is a white solid capable of existing in two crystalline forms, one of which melts at  $16^{\circ}$ , the other at  $50^{\circ}$ . It has an intense affinity for water, hissing loudly

when thrown into this liquid, and forming sulphuric acid with great elevation of temperature :—



### 51. SULPHURIC ACID.

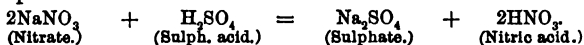
Symbol,  $\text{H}_2\text{SO}_4$ . Molecular weight, 98.

**Occurrence**—This acid is sometimes found in the free state in the waters of volcanic districts. The metallic sulphates form an important class of minerals, of which the best known are *gypsum* (calcium sulphate,  $\text{CaSO}_4$ ) and *heavy-spar* (barium sulphate,  $\text{BaSO}_4$ ).

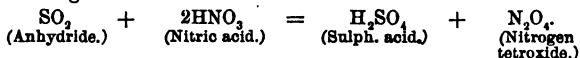
**Manufacture**.—The numerous instances in which this acid has been employed to effect chemical decompositions must already have impressed the student with the vast importance of this compound. Sulphuric acid is no less useful in the industrial arts than in the laboratory; hence vast quantities are manufactured annually in this country.

We have already noticed incidentally that sulphur dioxide has a great tendency to combine with a further quantity of oxygen. This affinity for oxygen is the basis of the production of sulphuric acid. The chemical changes occurring in the manufacture of the acid are thus represented in their simplest form :—

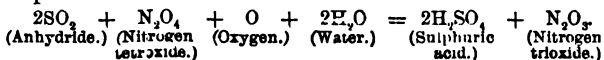
(1) Nitric acid is liberated from a nitrate by means of sulphuric acid :—



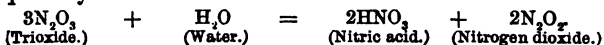
(2) Sulphurous anhydride produced from burning sulphur is brought into contact with this nitric acid :—



(3) Nitrogen tetroxide in presence of atmospheric oxygen and steam reacts upon a further quantity of sulphur dioxide :—



(4) Nitrogen trioxide is decomposed by a further quantity of steam :—



(5) Nitrogen dioxide takes up a further quantity of oxygen from the air, reproducing nitrogen tetroxide, which is again decomposed as before :—



It will be seen from these equations that a small quantity of nitric acid is capable of oxidising an indefinitely large quantity of sulphuric dioxide. At the end of the series of reactions we have, in fact, reached the same compounds ( $\text{HNO}_3$  and  $\text{N}_2\text{O}_4$ ) with which the oxidation was started in the first instance.

In practice the process is carried out in the following manner :—

(a) Crude sulphur, or iron-pyrites ( $\text{FeS}_2$ ), is burnt in a current of air in a furnace, in the centre of which is placed a small stove containing a mixture of nitre and sulphuric acid.

(b) The mixture of air, sulphur dioxide, and oxides of nitrogen thus produced is led through suitable flues into a series of leaden chambers supported on wooden beams. These chambers have steam continuously blown into them from several jets. The capacity of the leaden chambers is from 50,000 to 100,000 cubic feet.

(c) The sulphuric acid produced in the first chamber collects on the floor of that chamber, the unaltered gases passing on into the second chamber, where a further quantity of acid is produced; and so on. The residual gases are finally carried up a tower, where they are met by a further supply of steam, which removes acid vapours, the escaping gas being little else than atmospheric nitrogen. The acid collected in the chambers becomes weaker the further the chamber is removed from the furnace.

**Properties.**—The acid withdrawn from the first chamber has a specific gravity of 1.55 and contains about 65 per

cent. of real  $\text{H}_2\text{SO}_4$ . This is boiled down in leaden pans till the specific gravity is raised to 1.72, which corresponds to 79 per cent. of  $\text{H}_2\text{SO}_4$ . Further concentration is effected in glass or platinum retorts, the liquid finally attaining a specific gravity of 1.842. This concentrated acid is known in commerce as "oil of vitriol."

Sulphuric acid is a transparent oily liquid, colourless and inodorous. The commercial oil of vitriol is never absolutely pure, but always contains small quantities of lead (from the chambers), and sometimes arsenic (from the pyrites), oxides of nitrogen, &c. The acid which is left after concentration in the leaden pans is invariably of a dark brown colour, from the pressure of organic matter. Sulphuric acid possesses a strong affinity for water, absorbing moisture rapidly when exposed to the air. Its water-absorbing power has already been made use of for drying gases (see, for instance, p. 27). When brought in contact with certain organic substances containing carbon, hydrogen and oxygen, the elements of water, are withdrawn by sulphuric acid, leaving a carbonaceous residue. Hence sulphuric acid *chars* such substances as sugar and wood. The action of sulphuric upon oxalic and formic acids (p. 122) depends upon this great affinity for water. A mixture of sulphuric acid and water becomes hot when shaken: four parts of acid to one of water causes an elevation of temperature from  $0^\circ$  to  $100^\circ$ , the mixture when cool occupying a less volume than that of the joint volumes taken. Sulphuric acid decomposes when heated to redness, sulphur dioxide, water, and oxygen being the results:—



Sulphuric acid combines with water to form a hydrate ( $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ ), which crystallises out on cooling the mixture down to  $7^\circ$ . An acid of great strength, which fumes in the air, is obtained by distilling a sulphate of iron in earthen retorts. This is the source from which sulphuric acid was first obtained: it is known as "fuming" or "Nordhausen sulphuric acid," from the locality in which it was made. Its composition answers to that of a mole-

cule of sulphuric acid united with a molecule of sulphur trioxide ( $\text{H}_2\text{SO}_4 \cdot \text{SO}_3$ ).

Sulphuric acid is the hydrogen salt of a series of salts termed *sulphates*.

The remaining acids of sulphur are not of sufficient importance to occupy the student's attention at the present stage of his studies.

### 3. COMPOUND OF SULPHUR WITH CARBON.

#### 52. CARBON DISULPHIDE.

Symbol,  $\text{CS}_2$ . Molecular weight, 76.

**Preparation and Properties.**—This interesting substance is prepared by passing sulphur vapour over red-hot charcoal:—



It is a colourless liquid possessing a peculiar odour, and is exceedingly inflammable, burning with a pale blue flame, and giving off carbon and sulphur dioxides. Its boiling point is  $43.3^\circ$ ; its specific gravity is 1.27 (at  $15^\circ$ ). Carbon disulphide evaporates rapidly in the air, producing a great degree of cold. Its vapour, when mixed with nitrogen dioxide, burns with intense brilliancy. The vapour density referred to hydrogen is 38. Carbon disulphide is now largely used in the vulcanisation of india-rubber, and for other industrial purposes.

### 4. OTHER COMPOUNDS OF SULPHUR.

Sulphur forms compounds with chlorine, bromine, iodine, and fluorine, as well as with carbon and oxygen, carbon and chlorine, &c. For detailed accounts of these rarer compounds the student must refer to the larger works.

#### 53. SELENIUM.<sup>1</sup>

Symbol,  $\text{Se}$ . Atomic weight, 79.5.

This element occurs only in small quantities in nature, and is found in certain mineral sulphides. It is so closely allied to sulphur in its chemical characters that a detailed

<sup>1</sup> Named after *selene*, the mythological name of the moon.

account of its various compounds will be here unnecessary. Selenium, like sulphur, presents several modifications, some being amorphous and others crystalline; some being soluble in carbon disulphide, and others, like the plastic modification of sulphur, being insoluble in that liquid. Selenium burns with a blue flame in the air or in oxygen, giving off a most disagreeable odour, due to the dioxide. The most important compounds of this element are shown in the following list:—

Hydrogen selenide .....	$\text{H}_2\text{Se}$ .
Selenium dioxide .....	$\text{SeO}_2$ .
Selenious acid.....	$\text{H}_2\text{SeO}_3$ .
Selenic acid .....	$\text{H}_2\text{SeO}_4$ .
Carbon diselenide .....	$\text{CSe}_2$ .

#### 54. TELLURIUM.\*

Symbol, Te. Atomic weight, 129.

Tellurium is even a rarer element than selenium. It is found combined with gold or silver in Hungary, Transylvania, and in the Albany Mountains of California. It bears great superficial resemblance to a metal, exhibiting a bright white lustre. Tellurium burns in the air with a bluish green flame, giving off fumes of the dioxide.

Its chief compounds are the following:—

Hydrogen telluride .....	$\text{H}_2\text{Te}$ .
Tellurium dioxide.....	$\text{TeO}_2$ .
Tellurous acid .....	$\text{H}_2\text{TeO}_3$ .
Tellurium trioxide.....	$\text{TeO}_3$ .
Telluric acid .....	$\text{H}_2\text{TeO}_4$ .

**Summary.**—1. The sulphur group comprises the elements sulphur, selenium, and tellurium, which exhibit a gradation in atomic weight and chemical properties.

2. The elements of the sulphur group are related to oxygen in their chemical characters. They all form hydrides containing two atoms of hydrogen to one of the element.

3. Sulphur, selenium, and tellurium form dioxides and corresponding acids. Trioxides of sulphur and tellurium have been obtained. The corresponding acids of all three elements are known.

4. Sulphuric acid is produced by the oxidation of sulphur dioxide by atmospheric oxygen in presence of oxides of nitrogen and steam.

5. Sulphur dioxide is obtained by heating sulphuric acid with copper, mercury, or charcoal.

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\* Named after *tellus*, the mythological name of the earth.

## CHAPTER VIII.

## PHOSPHORUS AND ARSENIC.

THESE two elements, together with nitrogen and certain metals to be considered subsequently, form another natural group.

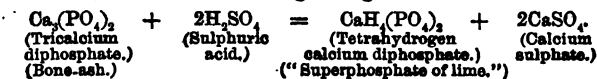
55. PHOSPHORUS.<sup>1</sup>

Symbol, P. Atomic weight, 31.

**Occurrence.**—Phosphorus is never found uncombined in nature, but always in combination with oxygen and a metal (chiefly calcium) as a metallic phosphate. *Apatite*, *phosphorite*, and *coprolites*<sup>2</sup> are minerals composed chiefly of calcium phosphate. The ash resulting from the ignition of bones (bone-earth) consists of calcium phosphate—animals deriving this substance from plants, and plants deriving it from the soil, in which it exists in small quantities, being derived from the primitive rocks by disintegration.<sup>3</sup> Combined phosphorus exists also in the brain, the blood, and in all the soft animal tissues.

**Manufacture.**—Phosphorus is made chiefly from bone-ash in the following manner:—

(1) Three parts of finely-powdered bone-ash are mixed with two parts of strong sulphuric acid and eighteen parts of water, when the following change occurs:—



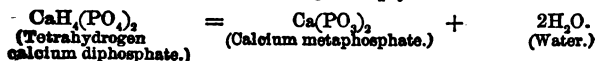
(2) The solution of "superphosphate" is filtered off from the insoluble calcium sulphate, evaporated down to a

<sup>1</sup> G. *phōs*, light; and *phērō*, I bear.

<sup>2</sup> G. *kopros*, dung; *lithōs*, stone. Applied to petrified excrements.

<sup>3</sup> See p. 129, note.

syrup, mixed with one-quarter of its weight of charcoal powder, and heated to a dull redness in an iron pot. The "superphosphate" at this stage simply loses water:—



(3) The mixture of calcium metaphosphate and charcoal dust is next distilled in an earthen retort at a bright red heat, when the phosphorus distils over and is allowed to drop into water. The reaction occurring at this stage is thus represented:—

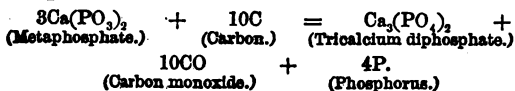


Fig. 27.

Manufacture of phosphorus.

The furnace employed is shown in the accompanying figure.

The copper tube *c* dips below the surface of the water in the receiver, while *t* only just passes through the neck, and serves to carry off the waste gases.

**Properties.**—Phosphorus is a yellowish, semi-transparent, wax-like solid, which usually occurs in commerce in the form of sticks. It is highly poisonous. Near the freezing point of water phosphorus becomes brittle, but in warm weather it is flexible and may be bent without breaking. At  $44^\circ$  it melts into an oily transparent liquid. Phosphorus possesses a great affinity for oxygen, combining slowly with this gas when exposed to the air at ordinary temperatures, and giving off a white vapour, which appears luminous in the dark. A little above its melting point it ignites and burns with an intense white flame, giving off white fumes of the pent-



oxide. The student will recall to mind that this power of combining with oxygen was made use of for preparing nitrogen from atmospheric air (see p. 46). The extreme inflammability of phosphorus renders it very dangerous of manipulation by the inexperienced. It should always be kept and cut under water. Phosphorus burns with intense brilliancy in oxygen gas: in nitrogen dioxide its flame is extinguished, if burning feebly, but if in a state of vigorous combustion it decomposes the oxide of nitrogen, and burns as brilliantly as in oxygen itself. The specific gravity of solid phosphorus is 1.823, and of the liquid, 1.763. Its boiling point is about  $290^{\circ}$ . Water does not dissolve phosphorus, but it is soluble in carbon disulphide, oil of turpentine, ether, and many other organic liquids. The solution in carbon disulphide, when allowed to evaporate in a thin film, takes fire spontaneously in the air.

**AMORPHOUS PHOSPHORUS.**—Phosphorus presents several modifications, of which the best known is that called *red* or *amorphous phosphorus*. This modification is prepared by heating the ordinary form of the substance for thirty or forty hours at a temperature of  $240^{\circ}$  in a flask filled with carbon dioxide or some other gas that has no action on phosphorus. This variety is much less active in its chemical characters than ordinary phosphorus. It does not oxidise in air at the ordinary temperature, nor does it ignite till heated above  $260^{\circ}$ , at which temperature it becomes converted into the ordinary modification. It usually presents the appearance of a dull red powder, having a specific gravity of 2.14.

Phosphorus has been already specified as an exception to the rule that the density of an element in the state of vapour is equal to its atomic weight. Its vapour density referred to hydrogen is 62—that is, it contains two atoms. Hence the volume occupied by the atom is one-half, and the molecule contains four atoms. Phosphorus was discovered by Brandt in 1669.

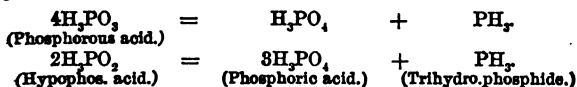
## 1. COMPOUNDS OF PHOSPHORUS WITH HYDROGEN.

## 56. TRIHYDROGEN PHOSPHIDE

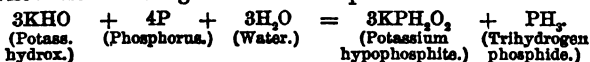
(Phosphoretted Hydrogen).

Symbol,  $\text{PH}_3$ . Molecular weight, 34.

**Preparation and Properties.**—Several processes are known for preparing this compound. It is produced in a pure state by heating either phosphorous or hypophosphorous acid:—



It is usually prepared by boiling together potassium hydroxide, water, and phosphorus in a glass flask or retort, when the following reaction takes place:—



Phosphoretted hydrogen is a colourless transparent gas possessing a most disagreeable odour and poisonous properties. As prepared by the last-given process it is spontaneously inflammable, each bubble bursting into a flame as it comes to the surface of the water, and giving rise to a beautiful ring of phosphorus pentoxide, which expands as it ascends. This spontaneous inflammability is supposed to be due to the presence of liquid phosphoretted hydrogen in the gas. This last compound is a highly inflammable liquid, having the formula  $\text{P}_2\text{H}_4$ . The density of the trihydride referred to hydrogen is 17.

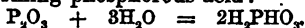
## 2. OXIDES AND OXYGEN ACIDS OF PHOSPHORUS.

Two oxides or anhydrides of phosphorus are known and several acids, of which the most important are named in the following list:—

Oxides.	Acids.
Phosphorus trioxide ... $\text{P}_2\text{O}_3$ .	Hypophosphorous acid ... $\text{H}_3\text{PH}_2\text{O}_2$ .
Phosphorus pentoxide $\text{P}_2\text{O}_5$ .	Phosphorous acid ..... $\text{H}_3\text{PHO}_3$ .
	Phosphoric acid ..... $\text{H}_3\text{PO}_4$ .
	Metaphosphoric acid ..... $\text{HPO}_3$ .
	Pyrophosphoric acid ..... $\text{H}_4\text{P}_2\text{O}_7$ .

**57. PHOSPHORUS TRIOXIDE.**Symbol,  $P_2O_3$ . Molecular weight, 110.

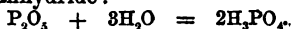
**Preparation.**—This oxide is produced when phosphorus undergoes slow combustion in a limited supply of air. It is a white volatile solid which combines energetically with water, forming phosphorous acid:—



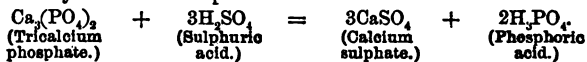
Phosphorous acid is also produced when phosphorus trichloride acts upon water (for reaction see p. 88). Phosphorous acid gives rise to a series of salts termed *phosphites*.

**58. PHOSPHORUS PENTOXIDE.**Symbol,  $P_2O_5$ . Molecular weight, 142.

**Preparation.**—When phosphorus is burnt with a full supply of air this oxide is given off in white flakes. It has a most powerful affinity for water, absorbing moisture rapidly from the air, and hissing like a red-hot piece of metal when thrown into water. The compound formed by the union of phosphorus pentoxide and water is phosphoric acid;<sup>1</sup> hence the pentoxide may be considered as phosphoric anhydride:—



Phosphoric acid is produced likewise by the action of water upon phosphorus pentachloride (for reaction, see p. 88); by the oxidation of phosphorus by means of nitric acid; and by the decomposition of a phosphate—such as bone-ash—by means of sulphuric acid:—



When the hydrogen of phosphoric acid is replaced by a metal, a salt termed a *phosphate* is produced.

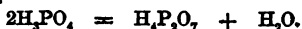
**59. METAPHOSPHORIC ACID** is produced when ordinary phosphoric acid is heated to redness, water being given off:—



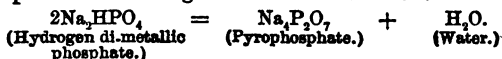
<sup>1</sup> The solution must be boiled to produce this acid.

This acid is connected with salts known as *metaphosphates*.

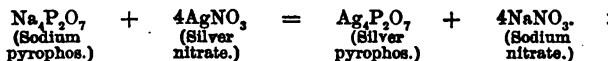
**60. PYROPHOSPHORIC ACID**<sup>1</sup> is obtained from ordinary phosphoric acid by heating this substance for some hours at 210°:—



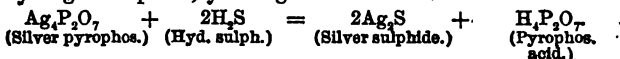
The pyrophosphates are obtained by heating ordinary phosphates containing two atoms of a metal:—



This sodium pyrophosphate undergoes decomposition when mixed with a lead or silver salt:—



The silver salt is in its turn decomposed in a current of hydrogen sulphide, yielding the free acid:—



### 3. COMPOUNDS OF PHOSPHORUS WITH THE HALOGENS.

The following is a list of these compounds so far as at present known:—

Phosphorus trichloride .....	$\text{PCl}_3$ .
Phosphorus pentachloride .....	$\text{PCl}_5$ .
Phosphorus tribromide .....	$\text{PBr}_3$ .
Phosphorus pentabromide .....	$\text{PBr}_5$ .
Phosphorus tri-iodide .....	$\text{PI}_3$ .
Phosphorus penta-iodide.....	$\text{PI}_5$ .
Phosphorus trifluoride .....	$\text{PF}_3$ .

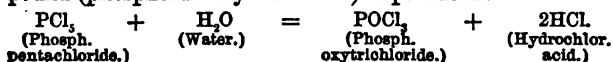
Of these compounds the chlorides only will be here considered. Phosphorus ignites spontaneously in chlorine, forming either the trichloride or the pentachloride according to the quantity of chlorine present.

**61. PHOSPHORUS TRICHLORIDE** is a transparent colourless liquid having a specific gravity of 1.45. It boils at 74° under ordinary atmospheric pressure and is decom-

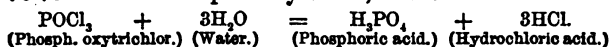
<sup>1</sup> G. pur, fire. Meaning the phosphoric acid obtained by heat.

posed by water (the reaction is given on p. 88); for which reason the liquid always fumes in the air, owing to the formation of hydrochloric acid. The molecular weight is 137.5.

**62. PHOSPHORUS PENTACHLORIDE** is a crystalline solid of a yellowish colour. Its molecular weight is 208.5 and its molecular volume anomalous, being a case of dissociation (p. 68). Its decomposition in presence of water has been already referred to (p. 88). If a limited quantity of water is present, however, another compound (phosphorus oxytrichloride) is produced:—



**63. PHOSPHORUS OXYTRICHLORIDE** is a colourless transparent liquid which fumes in the air. Its specific gravity is 1.7, and it boils at 110°. The molecular weight is 153.5, and the density of vapour referred to hydrogen 76.75. It is decomposed by water, thus:—



Phosphorus forms sulphides, selenides, and tellurides, besides a sulphotrichloride ( $\text{PSCl}_3$ ), a sulphotribromide ( $\text{PSBr}_3$ ), an oxytribromide ( $\text{POBr}_3$ ), and an oxydichlorobromide ( $\text{POCl}_2\text{Br}$ ); but these compounds will be found more fully described in the larger manuals.

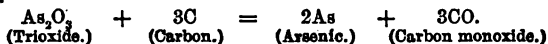
## 64. ARSENIC.

Symbol, As. Atomic weight, 150.

**Occurrence.**—This element is found in small quantities in the free state, but much more commonly associated with iron as *arsenical iron*, and with iron and sulphur as *arsenical pyrites*. Arsenic occurs also in combination with the metals cobalt and nickel, and in small traces in many mineral waters.

**Preparation.**—The arsenical ore is roasted in a furnace, whereby the arsenic is converted into the trioxide, which volatilises and is condensed in suitable flues. Arsenic

trioxide, when heated with charcoal, gives up its oxygen, thus :—



**Properties.**—Arsenic is a grey brittle substance which oxidises in the air. Its specific gravity varies from 4·7 to 5·96. At a dull red heat it volatilises without previous fusion; the vapour possesses a characteristic odour of garlic. When heated in the air arsenic burns with a blue flame, giving off white fumes of the trioxide. The poisonous nature of arsenical compounds is well known to all. The atomic volume of arsenic, like that of phosphorus, is only one-half the normal quantity.

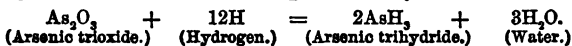
#### 1. COMPOUND OF ARSENIC WITH HYDROGEN.

##### 65. ARSENIC TRIHYDRIDE

(Arsenetted Hydrogen).

Symbol,  $\text{AsH}_3$ . Molecular weight, 78.

**Preparation.**—This gas is evolved when a soluble arsenical compound is introduced into a flask generating hydrogen from zinc and sulphuric or hydrochloric acid :—



**Properties.**—Arsenetted hydrogen is a colourless transparent gas of a most foetid odour, and is extremely poisonous. At  $-30^\circ$  it liquefies, but has not yet been solidified. The vapour density referred to hydrogen is 39. It burns in the air with a blue flame, forming water and arsenic trioxide, but if a piece of cold porcelain is held in the centre of the flame where the combustion is imperfect, arsenic is deposited in mirror-like stains, which are dissolved by a solution of sodium hypochlorite. This reaction serves as a test for the presence of arsenic. At a red heat arsenic trihydride is resolved into its constituents, so that if the tube through which the gas is passing is heated at one or two points, brilliant arsenical mirrors are deposited just in front of the heated portions.

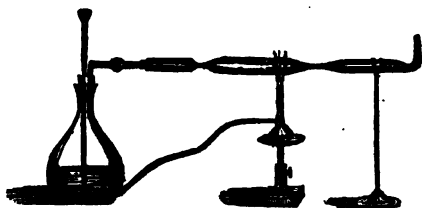


Fig. 28.—Arsenical mirrors from arsonetted hydrogen.

## 2. OXIDES AND ACIDS OF ARSENIC.

<i>Oxides.</i>		<i>Acids.</i>	
Arsenic trioxide .....	$\text{As}_2\text{O}_3$	Arsenious acid .....	$\text{H}_3\text{AsO}_2$
Arsenic pentoxide .....	$\text{As}_2\text{O}_5$	Arsenic acid .....	$\text{H}_3\text{AsO}_4$

## 66. ARSENIC TRIOXIDE.

Symbol,  $\text{As}_2\text{O}_3$ . Molecular weight, 198.

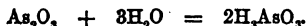
**Preparation.**—This oxide of arsenic occurs native in small quantities, but is prepared on a large scale by roasting ores containing arsenic, such as *arsenical pyrites* ( $\text{FeSAs}$ ). When arsenic burns in the air or in oxygen the trioxide is produced.

**Properties.**—Arsenic trioxide is a white solid possessing no odour. At  $218^\circ\text{C}$ . it volatilises, forming a colourless and inodorous vapour, the density of which referred to hydrogen is 198—being, in consequence, a departure from the well-known law of molecular volumes. Arsenic trioxide is slightly soluble in cold water, but dissolves more readily in hot water and in hydrochloric acid. This oxide is the “white arsenic” of commerce, and is extremely poisonous, a dose of two or three grains being fatal. Arsenic trioxide exists in two modifications, a crystalline and an amorphous. The amorphous or vitreous<sup>1</sup> oxide is produced by cooling the vapour of the oxide very gradually. It is a transparent solid of 3.74 specific gravity which

<sup>1</sup> That is, *glassy*. (*L. vitrum*, glass.)

becomes opaque and passes into the crystalline variety on keeping. The crystalline form is produced when the vapour of the oxide is cooled rapidly. It generally presents the appearance of octohedral crystals, having a specific gravity of 2.7.

The aqueous solution of arsenic trioxide is supposed to contain the arsenious acid, corresponding to phosphorous acid:—

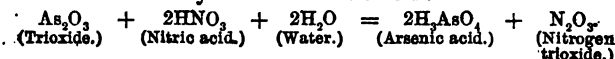


This acid is connected with a series of salts called *arsenites*, “Scheele’s green” being a copper arsenite and “Fowler’s solution” being a solution of potassium arsenite.

### 67. ARSENIC PENTOXIDE.

Symbol,  $\text{As}_2\text{O}_5$ . Molecular weight, 230.

**Preparation.**—Arsenic acid is produced by oxidising arsenic trioxide by means of nitric acid:—



Arsenic acid when heated to  $270^\circ$  loses water and leaves the pentoxide:—



**Properties.**—The pentoxide or arsenic anhydride is an amorphous white powder not so poisonous as the trioxide. At a red heat it decomposes into  $\text{As}_2\text{O}_3$  and  $\text{O}_2$ . It dissolves slightly in water, forming arsenic acid, which is the hydrogen salt of the *arsenates*. Compounds corresponding to meta- and pyrophosphoric acids are said to exist, viz., metarsenic acid ( $\text{HAsO}_3$ ) and pyarsenic acid ( $\text{H}_4\text{As}_2\text{O}_7$ ).

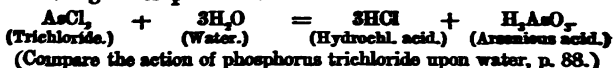
### 3. COMPOUNDS OF ARSENIC WITH THE HALOGENS.

Arsenic trichloride .....	$\text{AsCl}_3$
Arsenic tribromide .....	$\text{AsBr}_3$
Arsenic triiodide .....	$\text{AsI}_3$
Arsenic trifluoride .....	$\text{AsF}_3$

Finely-divided arsenic ignites spontaneously in chlorine, forming the trichloride, which is a heavy oily liquid boiling



at  $132^{\circ}$ . Its specific gravity is 2.2 and its vapour density 90.75 ( $H = 1$ ). In presence of water it undergoes the following decomposition:—



#### 4. COMPOUNDS WITH ARSENIC OF SULPHUR.

Arsenic disulphide (realgar)... $\text{As}_2\text{S}_2$		Sulpharsenious acid $\text{H}_2\text{AsS}_2$
Arsenic trisulphide (orpiment) $\text{As}_2\text{S}_3$		
Arsenic pentasulphide ..... $\text{As}_2\text{S}_5$		Sulpharsenic acid ... $\text{H}_2\text{AsS}_5$

When sulphuretted hydrogen is passed through an acid solution of the trioxide arsenic trisulphide is precipitated as a bright yellow powder:—



Realgar and orpiment are found native: the pentasulphide has not yet been definitely obtained in the free state. Sulpharsenious and sulpharsenic acids are the hydrogen salts of the *sulpharsenites* and *sulpharsenates* respectively.

**Summary.**—1. Phosphorus and arsenic are allied to one another and to nitrogen in their chemical characters. They all three form hydrides containing three atoms of hydrogen to one of the element.

2. Phosphorus, arsenic, and nitrogen form oxides and oxygen acids: each of these elements forms a trioxide and a pentoxide.

3. Phosphorus is manufactured from bone-earth by converting this substance first into a "superphosphate," then into a metaphosphate, and finally igniting the metaphosphate with charcoal.

4. A soluble compound of arsenic introduced into a flask generating hydrogen gives rise to the formation of arsenetted hydrogen, the flame of which deposits an arsenical mirror upon cold porcelain. This mirror is dissolved by sodium hypochlorite.

5. An acid solution of an arsenical compound gives a yellow precipitate of arsenic trisulphide when treated with sulphuretted hydrogen.

## CHAPTER X.

THE ATOMIC THEORY (*Continued*).

## A.—THE ELECTRO-CHEMICAL THEORY.

(a) **Electrolysis.**—The student has already had occasion to use an electric current for the resolution of water into its elements (p. 19); the study of this decomposing action of electricity, although belonging more properly to the science of *Physics*, must be here briefly resumed.

The electrical decomposition of a compound is termed *electrolysis*,<sup>1</sup> and the decomposed compound is termed the *electrolyte*. An electrolyte must be a conductor of electricity, and must be presented to the current in the liquid state—either dissolved in water or fused by heat.

The fundamental law of electrical action is, “that bodies similarly electrified repel each other, while bodies dissimilarly electrified attract each other.” In accordance with this law, those elements which appear at the positive pole of a battery are termed *electro-negative*—those which appear at the negative pole are called *electro-positive*.



Fig. 29.

is hydrochloric acid.

The upper brackets show the grouping of the atoms in the chain of molecules *before* the liberation of the terminal

The accompanying figure represents the state of affairs when a binary compound is undergoing electrolysis. The positive pole (where the current enters) is marked *p*, the negative pole (where the current leaves the solution) is marked *n*. The electrolyte

<sup>1</sup>. G. *ēlektrōn*, amber (the original source of electricity), and *lūō*, I liberate.

H and Cl atoms—the lower brackets show the grouping after the evolution of the terminal atoms.

After the discharge of these terminal atoms the chain of molecules is supposed to undergo rearrangement, so as to present the electro-negative element to the positive pole; and *vice versâ*.

(b) **Electro-chemical Classification.**—The division of the elements into positive and negative as above pointed out must not be regarded as an absolute division. The same element may be positive or negative according to the nature of the element to which it is presented. Two positive or two negative elements may combine together, but the union is never so energetic as when a positive combines with a negative element. In this latter case the more widely the elements differ in their electrical relations, the more energetic is their union—the greater is the amount of heat and light produced—the greater is the *affinity* which the elements are said to possess for each other.

The following elements are more or less negative towards the remaining elements :<sup>1</sup>—

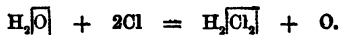
Fluorine.	Oxygen.
Chlorine.	Sulphur.
Bromine.	Selenium.
Iodine.	Tellurium.

#### B.—CHEMICAL EQUIVALENCE.

(a) **Substitution.**—In studying the various reactions which we have had occasion to represent symbolically the student will probably have observed that the atoms of the different elements have in many cases different replacing values. When one element replaces another in a chemical reaction a *substitution* is said to take place—in the decomposition of steam by chlorine at a red heat,

<sup>1</sup> This list is from Dr. Frankland's "Lecture Notes for Chemical Students," vol i., p. 4.

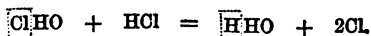
for example (p. 25), chlorine may be said to be *substituted* for the oxygen in water, thus :—



In hydrochloric acid, therefore, *two* atoms of chlorine are *equivalent* to the *one* atom of oxygen in water. So also, on considering the decomposition of ammonia by chlorine (p. 65).:—



—we see that *three* atoms of chlorine are capable of being substituted for *one* atom of nitrogen. Now, in hydrochloric acid itself one atom of chlorine is combined with one atom of hydrogen; and as this is the only known combination of hydrogen with chlorine, we may say (and the statement is borne out by a large body of facts) that one atom of chlorine is *equivalent* to, or is capable of being *substituted* for, one atom of hydrogen. This is seen when hydrochloric acid acts upon hypochlorous acid (p. 93.):—



From this it follows that one atom of oxygen is equivalent to *two* atoms of hydrogen, and one atom of nitrogen equivalent to *three* atoms of hydrogen. Expressing this fact in terms of the atom-weights of the respective elements, we should say that one atom or 16 parts by weight of oxygen are equivalent to two atoms or two parts by weight of hydrogen, or eight parts by weight of oxygen are equivalent to one part by weight of hydrogen.

With regard to nitrogen, we should say that 14 parts by weight are equivalent to three parts by weight of hydrogen, or that  $\frac{14}{3} = 4\frac{2}{3}$  parts are equivalent to one part of hydrogen. These numbers—8 and  $4\frac{2}{3}$ —are the *equivalents* of oxygen and nitrogen respectively, so that the equivalent of an element may be defined as *the smallest proportion by weight that can replace or combine with one atom of hydrogen chlorine, or an equivalent element.*

(b) **Atomicity.**—The smallest *chemically indivisible* weight of an element—hydrogen being considered as unity—we have designated an *atom*; the smallest weight that replaces or combines with one atom of hydrogen, chlorine, &c., we have learnt to call an *equivalent*.

Now, if the atomic weight of an element be divided by its equivalent weight, the quotient expresses the number of hydrogen or chlorine atoms capable of combining with one atom of that particular element.

Thus, oxygen is capable of combining with  $\frac{16}{8} = 2$  atoms of hydrogen or chlorine, 16 being the atomic and 8 the equivalent weight of oxygen. This atom-fixing power is termed the *atomicity* of an element; and an element whose atom combines with *one* atom of hydrogen or an equivalent element is called a *monad*, with *two* atoms a *dyad*, with *three* atoms a *triad*; and so on. The atomicity of an element can thus be determined by ascertaining the number of hydrogen or chlorine atoms with which it combines—the atomic weight of an element divided by its atomicity gives its equivalent value. Thus:—

Oxygen .....	$\frac{16 \text{ (atomic weight)}}{2 \text{ (atomicity)}} = 8 \text{ equivalent.}$	
Sulphur .....	$\frac{32 \text{ (atomic weight)}}{4 \text{ (atomicity)}} = 8$	"
Phosphorus.....	$\frac{31 \text{ (atomic weight)}}{5 \text{ (atomicity)}} = 6\frac{1}{5}$	"

(c) **Classification according to Atomicity.**—In studying the non-metallic elements and their compounds in the preceding chapters we found it convenient to form the elements into groups the members of which possessed certain characters in common. Of these common characters *atomicity* is the most important for our present purpose. We see from this point of view why sulphur, selenium, and tellurium form oxides and hydrides of similar composition: it is because they have similar atom-fixing powers. So also with the halogen elements, which, being monads, form a series of hydrides containing one atom of hydrogen to one of the

element; while nitrogen, phosphorus, and arsenic, being triads, form trihydrides analogous to ammonia. In the following table the elements are classified according to their atomicity and also by horizontal lines into sections, the component members of which are closely related to each other in their characters:<sup>1</sup>—

MONADS.	DYADS.	TRIADS.	TETRADES.	PENTADS.	HEXADS.
Hydrogen	Oxygen	Boron	Carbon Silicon	Nitrogen	Sulphur Selenium Tellurium
Fluorine Chlorine Bromine Iodine	Calcium Strontium Barium	Gold Thallium	Titanium Tin	Phosphorus Arsenic	Chromium Manganese Iron
Lithium Sodium Potassium Rubidium Cæsium	Glucinum Thorium Yttrium Lanthanum Didymium Erbium		Aluminium Zirconium	Vanadium Antimony Bismuth	Molybdenum Tungsten
Silver	Magnesium Zinc Cadmium		Cobalt Nickel Cesium Indium Uranium	Niobium Tantalum	Ruthenium Osmium
	Copper Mercury		Lead Rhodium Palladium Platinum Iridium		

In this table the elements in each vertical column are *equivalent* to each other—can replace each other atom for atom. Thus, the hydrogen of hydrochloric acid might be replaced by an atom of any element in the same column. The following compounds are, in fact, known:—

HCl.	ICl.	LiCl.	NaCl.
(Hydrochl. acid.)	(Iodine chloride.)	(Lithium chlor.)	(Sodium chlor.)
RbCl.	CsCl.	KCl.	AgCl.
(Rubidium chlor.)	(Cæsium chlor.)	(Potassium chlor.)	(Silver chlor.)

To take another illustration from the tetradic group of elements:—

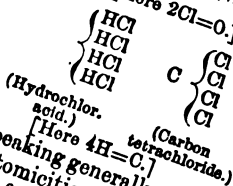
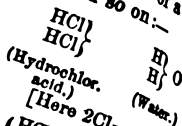
CCl <sub>4</sub> .	SiCl <sub>4</sub> .	TiCl <sub>4</sub> .	SnCl <sub>4</sub> .	PtCl <sub>4</sub> .
(Carbon, silicon, titanium, tin, and platinum tetrachlorides.)				

So also is one atom of a dyad equivalent to two atoms of

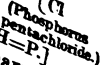
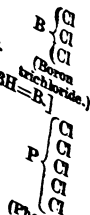
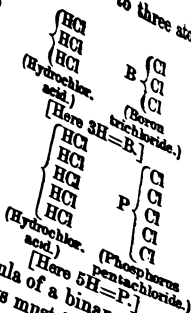
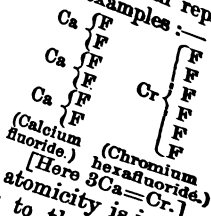
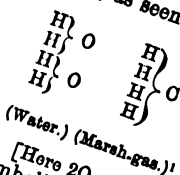
<sup>1</sup> In this table the *maximum* atomicity is assigned to each element.

# MONADIC ELEMENTS.

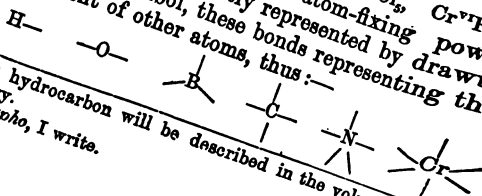
A monad, one atom of a triad equivalent to three atoms of a monad, and so on:—



Speaking generally, in the formula of a binary compound the atomicities of the two elements must be equal. From this it follows that two dyad atoms can replace one tetrad atom, while two triad or three dyad atoms can replace one hexad atom, as seen in the following examples:—



In symbolic notation the idea of atomicity is introduced by placing small Roman numerals to the right of the symbol, thus:—  
 $\text{HCl}^{\text{I}}$ ,  $\text{H}_2\text{O}^{\text{II}}$ ,  $\text{H}_3\text{N}^{\text{III}}$ ,  $\text{H}_4\text{C}^{\text{IV}}$ ,  $\text{P}^{\text{V}}\text{Cl}_5$ ,  $\text{Cr}^{\text{VI}}\text{F}_6$ .  
 (d) **Graphic Notation.**—The atom-fixing power of an element can be conveniently represented by drawing short lines from the symbol, these bonds representing the points of attachment of other atoms, thus:—



<sup>1</sup> This hydrocarbon will be described in the volume on Organic Chemistry.  
<sup>2</sup> G. grapho, I write.

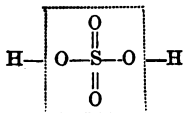
This mode of notation, first introduced by Crum-Brown, and adopted by Dr. Frankland,<sup>1</sup> is of great service in showing the *structure* or *constitution* of complex molecules—that is to say, the manner in which the elements are combined with one another. Such formulæ are known, therefore, as *graphic*, or *structural*. To illustrate the use of this notation, let us take a compound whose mode of decomposition we have already familiarised ourselves with, selecting for this purpose sulphuric acid. We have seen (p. 35) that when zinc or iron is presented to this acid its hydrogen becomes displaced, while the group  $\text{SO}_4$  remains combined with the metal as a sulphate. From this point of view we should formulate the acid *constitutionally*, thus:—



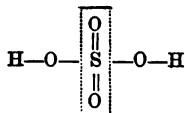
When sulphur dioxide is dissolved in water containing hydrogen dioxide or hydroxyl (to be considered in the next chapter) in solution sulphuric acid is produced:—



From this point of view we must therefore assign a different constitutional formula to sulphuric acid—we must regard it as a compound of sulphur dioxide with hydrogen dioxide. Both these constitutional formulæ are expressed if we represent the compound graphically:—



(Corresponding to  $\text{SO}_4\text{H}_2$ )



(Corresponding to  $\text{SO}_2(\text{HO})_2$ )

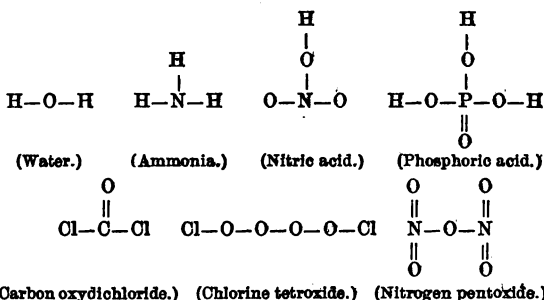
Thus are graphic formulæ of great service in showing the manner in which the elements in a compound are grouped together, the mode of grouping being deduced from the study of a large number of the chemical changes which the compound is capable of undergoing. In using these graphic formulæ the student must, however, guard

<sup>1</sup> See "Lecture Notes for Chemical Students," vol. i., chap. iii.



against the notion that they are magnified representations of the molecules. He must regard such a formula as nothing more than an *artificial epitome* of the reactions of a compound, indicating that the elements are grouped together in such and such a manner, that the compound when decomposed separates into such and such groups, and pointing out that when it is possible to bring these particular groups together the compound can in a large number of cases be built up or synthesized:

Other examples of graphic formulæ are given below:—

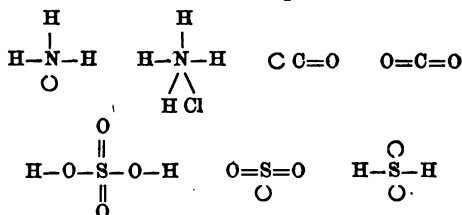


In constitutional formulæ the element having the highest atomicity is generally the grouping atom.

(e) **Variation of Atomicity.**—The atomicity of an element is not always a fixed quantity, but is liable to variation. In ammonia, for example, one atom of nitrogen is combined with three atoms of hydrogen; and the nitrogen is in consequence triadic, while its equivalent is  $\frac{1}{3}^4 = 4\frac{2}{3}$ . In ammonium chloride the nitrogen atom is combined with five monad atoms and is therefore pentatomic, its equivalent becoming  $\frac{1}{5}^4 = 2\frac{4}{5}$ . Similarly, carbon is a dyad in carbon monoxide and a tetrad in carbon dioxide, while sulphur is hexadic in sulphuric acid, tetradic in sulphur dioxide, and dyadic in sulphuretted hydrogen. These facts are expressed by the following formulæ:—



It is to be observed that an increase or diminution of atomicity generally takes place by an *even number* of bonds; hence Dr. Frankland explains this variation in atomicity by supposing that the two bonds of an atom can *combine with one another* and thus become *latent*.<sup>1</sup> These latent bonds would be thus introduced into the graphic formula of the above compounds:—



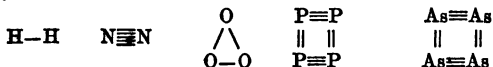
The number of atom-fixing units actually employed in linking an atom to other atoms Dr. Frankland terms the *active atomicity* of an element; the maximum number of bonds is termed the *absolute atomicity*. The sum of the *latent* and *active* bonds gives therefore the absolute atomicity of an element. An atom having its entire number of bonds active is said to be *saturated*, when latent bonds exist the compound is *unsaturated*. Thus, carbon monoxide is an unsaturated molecule, while carbon dioxide is saturated; the carbon in the former compound consequently unites *directly* with two other monad atoms (as in  $\text{COCl}_2$ ), or with one other dyad atom (as in  $\text{CO}_2$ ), while the carbon in carbon dioxide cannot be made to unite directly with any other element.

The polyatomic structure of most elementary molecules (see table, p. 13) is well explained by the theory of atomicity. Such atoms as  $\text{H}-$ ,  $\text{Cl}-$ ,  $\text{N}\equiv$  cannot exist singly in the free state because their bonds are unsaturated. The structure of such molecules with that of the triatomic molecules of ozone and the tetratomic molecules of phos-

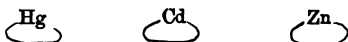
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<sup>1</sup> L. *latens*, hidden.

phorus and arsenic would be thus represented graphically :—



On the other hand, it is conceivable that an atom of a dyad element might exist singly in the free state, its two bonds satisfying each other. It is significant that the only known monatomic molecules are those of dyad elements; viz. :—



Several reactions that have come under the student's notice exemplify this tendency of the atoms of the *same element* to combine with one another. (See the reaction between hydrochloric and hypochlorous acid, p. 93 and the reaction between sulphurous acid and sulphuretted hydrogen, p. 142.)

An element in the nascent state is, as we have already seen (p. 87), more active than under ordinary conditions. This is because the atoms have not yet combined with one another to form molecules, so that they are more ready to take up the atoms of other elements.

**Compound Radicals.** If an atom be withdrawn from a saturated compound it is obvious that an unsaturated group of elements will be left. In many cases such an unsaturated group plays the part of an elementary body in chemical reactions and is then known as a *compound radical*. A compound radical, like an element (or *simple radical*), combines directly with other atoms and can be transferred without breaking up from one compound to another. It is in organic chemistry that we shall meet with the most numerous illustrations of compound radicals, comparatively few being known among inorganic compounds.

According to the number of its unsaturated bonds, a compound radical may be a monad, dyad, triad, tetrad, &c.

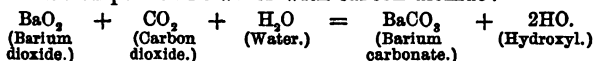
Consider, for instance, such a saturated molecule as that of water :—



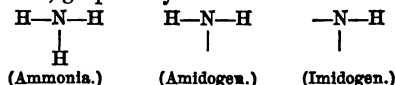
If one hydrogen atom be withdrawn, an unsaturated compound is left :—



This monad radical—known as *hydroxyl*—has actually been obtained in the free state by acting on barium dioxide suspended in water with carbon dioxide :—

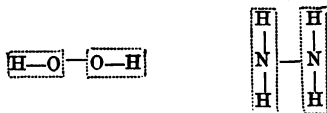


Similarly, ammonia ( $\text{NH}_3$ ) gives rise to the monad radical ( $\text{NH}_2$ )<sup>i</sup> known as *amidogen*, and by the withdrawal of two hydrogen atoms to the dyad radical *imidogen* ( $\text{NH}$ )<sup>ii</sup>. Thus, graphically :—



These last radicals are not known in the free state, but only in combination. Hence the fact of having been isolated<sup>1</sup> is by no means essential in order to constitute an unsaturated group a compound radical.

Just as an element having an odd number of bonds exists as a polyatomic molecule in the free state, so does a compound radical, when isolated, combine with itself so as to satisfy its vacated bonds. Thus, hydroxyl and amidogen (supposing the radical to have been isolated) would double themselves in the following manner :—

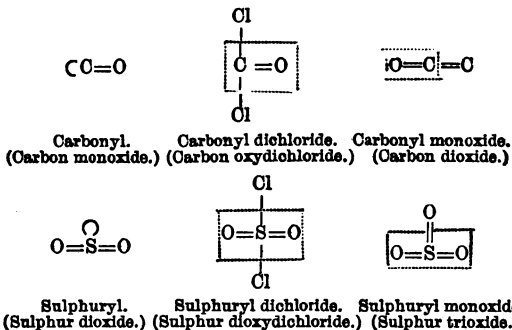


Hydroxyl (molecule.)      Amidogen (molecule.)

On the other hand, it is conceivable that a dyad radical, like a dyad element, might exist in the free state uncom-

<sup>1</sup> Obtained in the free state. (Fr. *isolé*, separate.)

bined, its two bonds satisfying one another. Carbon monoxide or *carbonyl*, and sulphur dioxide or *sulphuryl*, act in this manner as dyad radicals, combining directly with 2 monad or 1 dyad atom, thus :—



In studying such radicals as these last the student meets with a set of conditions of frequent occurrence in chemical science. A familiar compound becomes introduced to his notice under a new form—assumes, as it were, a new guise—and thereby becomes imbued with a new interest.

**Summary.**—1. The elements may be divided into classes, electro-positive and electro-negative, according as they appear at the negative or positive pole of a voltaic battery when their compounds are electrolysed.

2. The smallest proportion by weight of an element, *either integral or fractional*, that combines with, or can be substituted for, one part by weight of hydrogen, is the *equivalent weight*.

3. The *atomicity* of an element is a quantity expressing the number of atoms of hydrogen, or of an equivalent element capable of saturating one atom of such an element, and is obtained by dividing the *atomic* by the *equivalent* weight of the element.

4. An atom capable of combining with 1, 2, 3, &c., atoms of hydrogen is termed a *monad*, *dyad*, *triad*, &c. Elements with even atomicity are termed *artiads*<sup>1</sup>; those with an odd atomicity are called *perissads*<sup>2</sup>.

<sup>1</sup> G. *artios*, even.

<sup>2</sup> G. *perissos*, odd.

5. The atomicity of an element is often a variable quantity, but the increase or diminution in the number of atom-fixing units *generally takes place by an even number*. This is explained by supposing that a pair of atom-fixing units can satisfy each other.

6. The maximum atomicity of an element is its *absolute atomicity*; the number of atom-fixing units actually engaged by other atoms is the *active atomicity*, and the units saturating one another constitute the *latent atomicity*. An atom whose absolute atomicity is satisfied is *saturated*; where latent atomicity exists it is *unsaturated*.

7. An unsaturated group of elements playing the part of a single element is a *compound radical*. According to the number of its unsatisfied units, a compound radical is a monad, dyad, &c.

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## APPENDIX I.

### THE CONVERSION OF THERMOMETRIC SCALES.

THE thermometer<sup>1</sup> is an instrument for measuring temperature; the form most commonly used in the laboratory is the *mercurial thermometer*, so called because its indications are afforded by the expansion or contraction of a thread of mercury. It consists of a glass tube of capillary bore, having a bulb at one end, and being hermetically sealed at the other: the bulb and portion of the tube are filled with mercury, the remainder of the tube being vacuous, or, more correctly speaking, filled with mercury vapour. Two fixed points of temperature are by universal usage selected for the starting points of the graduation of the mercury column. These points are the freezing point of water, and (in this country) the boiling point of this same liquid under a pressure of 29·905 inches of mercury at the temperature of the freezing point of water. The exact position of the mercury in the tube having been marked at these two points, the space between them is divided into equal portions called *degrees*. There are three thermometric scales in use—that of Fahrenheit's (used only in this country), that of Celsius, or the Centigrade scale (used in France); and that of Reaumur (used largely in Germany). In Fahrenheit's scale the freezing point is made 32°, and the boiling point 212°; the Centigrade scale (as its name implies) makes the freezing point 0°, and the boiling point 100°; in Reaumur's scale the freezing point is 0°, and the boiling point 80°. Thus the space between the freezing and boiling points is in the three scales respectively divided into 180, 100, and 80 degrees; so that—

$$180^{\circ} \text{ F.} = 100^{\circ} \text{ C.} = 80^{\circ} \text{ R.};$$

or more simply—

$$9^{\circ} \text{ F.} = 5^{\circ} \text{ C.} = 4^{\circ} \text{ R.}$$

Bearing in mind that the freezing point of Fahrenheit's scale is 32°, we have the following rules for converting these scales into one another:—

1. F. to C.—Subtract 32, multiply by 5, and divide by 9.
2. C. to F.—Multiply by 9, divide by 5, and add 32.
3. F. to R.—Subtract 32, multiply by 4, and divide by 9.
4. R. to F.—Multiply by 9, divide by 4, and add 32.
5. R. to C.—Multiply by 5 and divide by 4.
6. C. to R.—Multiply by 4 and divide by 5.

Expressing these rules for conciseness as formulæ, we have—

$$\begin{array}{lll} \text{C.} = (\text{F.} - 32) \frac{5}{9} \dots 1 & \text{F.} = \frac{9\text{C.}}{5} + 32 \dots 2 & \text{R.} = (\text{F.} - 32) \frac{4}{9} \dots 3. \\ \text{F.} = \frac{9\text{R.}}{4} + 32 \dots 4 & \text{C.} = \frac{5\text{R.}}{4} \dots 5 & \text{R.} = \frac{4\text{C.}}{5} \dots 6. \end{array}$$

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<sup>1</sup> G. *Thermē*, heat *mētrōn*, a measure.



## APPENDIX II.

## THE FRENCH METRIC SYSTEM.

The starting point of this system is a measure of length termed the *mètre*, equal to 39·37079 inches. The *mètre* was originally chosen as being  $\frac{1}{10000000}$  of the length of the distance from the equator to the pole as measured along the earth's surface. The measurement of the earth adopted was that made by the French geometers, Delambre and Mechain. Subsequent research having, however, proved this measurement to be incorrect, the *mètre* is in reality the length of the platinum bar preserved in Paris, and is not referable to the terrestrial globe as a standard.

The Metric System being a decimal one, offers particular advantages for the purposes of calculation. The division of the *mètre* into tenths, hundredths, and thousandths is effected by the Latin prefixes *deci.*, *centi.*, and *milli.*; and its multiplication by ten, one hundred, and one thousand, is effected by the Greek prefixes *deca.*, *hecto.*, and *kilo.* Thus we have—

## Mètre.

Decimètre = $\frac{1}{10}$ mètre.	Decamètre = 10 mètres.
Centimètre = $\frac{1}{100}$ mètre.	Hectomètre = 100 mètres.
Millimètre = $\frac{1}{1000}$ mètre.	Kilomètre = 1,000 mètres.

The measures of surface are obtained by squaring the *mètre* and its derivatives :—

Decimètre square = $\frac{1}{100}$ mètre square.
Centimètre square = $\frac{1}{10000}$ mètre square.
Millimètre square = $\frac{1}{1000000}$ mètre square.

For the measurement of large surfaces (as in land surveying) the *are*, equal to 100 square mètres, is made the unit :—

Are = 100 mètres square.	
Deciare = $\frac{1}{10}$ Are = 10 mètr. square.	
Centiare = $\frac{1}{100}$ Are = 1 mètr. square.	
Milliare = $\frac{1}{1000}$ Are = $\frac{1}{10}$ mètr. square.	
Decare = 10 ares = 1,000 mètr. square.	
Hectare = 100 ares = 10,000 mètr. square.	
Kilare = 1,000 ares = 100,000 mètr. square.	

The measures of capacity and cubic measures are obtained by cubing the linear measures, thus :—

## Cubic decimètre or litre.

Decilitre = $\frac{1}{10}$ litre or 100 cubic centimètres.
Centilitre = $\frac{1}{100}$ litre or 10 cubic centimètres.
Millilitre = $\frac{1}{1000}$ litre or cubic centimètre.

Cubic mètre or stère.

Centistère =  $\frac{1}{100}$  stère or 10 litres (decalitre).

Decistère =  $\frac{1}{10}$  stère or 100 litres (hectolitre).

Stère or cubic mètre = 1,000 litres (kilolitre).

Decastère = 10 stères or 10,000 litres (myriolitre).

For measures of weight the *gramme*—the weight of one cubic centimètre of distilled water at its point of maximum density, 4°C—is chosen as unit:—

Gramme.

Decigramme =  $\frac{1}{10}$  grm.      Decagramme = 10 grms.

Centigramme =  $\frac{1}{100}$  grm.      Hectogramme = 100 grms.

Milligramme =  $\frac{1}{1000}$  grm.      Kilogramme = 1,000 grms.

Myriogramme = 10,000 grms.

We now subjoin a table showing the value of the most important units of the Metrical System in English weights and measures. The value of the multiples and sub-multiples of these units can, of course, be obtained by shifting the decimal point to the right or left, as the case may be.

TABLE SHOWING THE ENGLISH VALUE OF THE UNITS OF THE METRICAL SYSTEM.

Mètre = 39·37079 in. = 3·28099 ft. = 1·09363 yards = ·000621 miles.

1 inch = 2·540 centimètres.      1 yard = 0·914 mètre.

1 foot = 3·048 decimètres.      1 mile = 1·609 kilomètre.

Are = 1076·42993 square feet = 119·60332 sq. yards = 3·95383 poles = ·024711 acres.

1 sq. inch = 6·451 sq. centimètres.      1 sq. yard = 0·836 centiare.

1 sq. foot = 9·290 sq. decimètres.      1 acre = 0·404 hectare.

Litre = 61·02705 cubic inches = ·03531 cubic feet = 1·76077 pints = ·02751 bushels.

1 cubic inch = 16·386 cubic centimètres.

1 cubic foot = 28·315 cubic decimètres.

1 gallon = 4·543 litres.

Gramme = 15·43235 grains = ·03215 ounces (Troy) = ·00220 lbs. (Avoirdupois) = ·000000984 tons.

1 grain = ·065 gramme.      1 lb. Avd. = 0·453 kilogramm.

1 ounce Troy = 31·103 gramme.      1 cwt. = 50·802 kilogramm.

### APPENDIX III.

#### FRANKLAND'S NOTATION.

This notation, used in the laboratories of the Science and Art Department, is well adapted for representing the constitution of chemical compounds, and will be found, therefore, of particular

service in Organic Chemistry. In this notation the following compound radicals are recognized :—

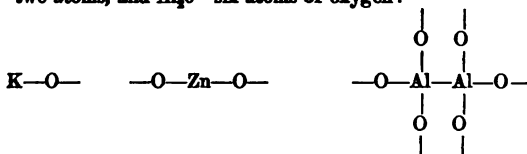
	Molecular Formulae.		Atomic Formulae.		Abbreviated Atomic Formulae.
Hydroxyl.....	(HO) <sub>2</sub>	...	HO	...	Ho*
Hydrosulphyl...	(HS) <sub>2</sub>	...	HS	...	Hs*
Ammonium.....	(NH <sub>4</sub> ) <sub>2</sub>	...	NH <sub>4</sub>	...	Am?
Ammonoxyl ...	(NH <sub>4</sub> O) <sub>2</sub>	...	NH <sub>4</sub> O	...	Amo.
Amidogen .....	(NH <sub>2</sub> ) <sub>2</sub>	...	NH <sub>2</sub>	...	Ad.

[Those marked \* have been obtained in the free state.]

In addition to these, certain compounds of the metals with oxygen are considered as radicals :—

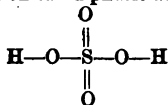
KO	abbreviated into Ko
ZnO <sub>2</sub>	" " Zno"
Al <sub>2</sub> O <sub>3</sub>	" " Al <sub>2</sub> O <sup>vi</sup>
&c.	&c.

In radicals of this class the number of oxygen atoms is always equal to the atomicity of the radical. Thus Ko contains one atom, Zno" two atoms, and Al<sub>2</sub>O<sup>vi</sup> six atoms of oxygen :—

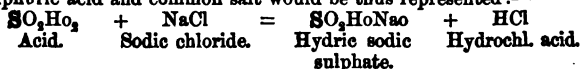


The multiplication of these radicals is effected by small figures below and to the right of the symbols. Thus Ho<sub>2</sub> stands for two semi-molecules of hydroxyl or (HO)<sub>2</sub>; Bao"<sub>3</sub> means three semi-molecules of baroxyl or 3BaO<sub>2</sub>, &c., &c.

In constitutional formulæ, written according to this notation, the first symbol or grouping element is printed in thick type. Such a symbol signifies that the atom is directly united with all the *active bonds* (see p. 167) of the atoms in the same line with it; and, as a rule, it is the atom of highest equivalence in the compound that occupies this position. Thus, from previous considerations, we represented the constitution of sulphuric acid :—

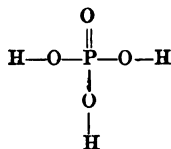
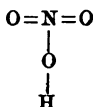


This would be formulated SO<sub>2</sub>Ho<sub>2</sub>, corresponding to its formation from sulphur dioxide and hydroxyl (p. 169). The reaction between sulphuric acid and common salt would be thus represented :—



Thick letters are not used unless the element have a higher atomicity than one.

Similarly with nitric acid and with phosphoric acid, the graphic formulae of which are:—



These acids would be thus formulated:—



In this notation the basicity of an acid corresponds to the number of semi-molecules of hydroxyl contained in it, and a salt is regarded as being derived from an acid by the substitution of a metallic compound radical for hydroxyl, thus:—

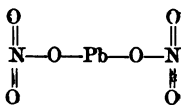
Acid.	Acid Salt.	Normal Salt.
<b>NO<sub>2</sub>Ho</b> .....	—	<b>NO<sub>2</sub>Ko</b>
Nitric.		Potassic nitrate.
" .....	—	<b>N<sub>3</sub>O<sub>4</sub>Pbo</b> " <sup>2</sup>
" .....	—	Plumbic dinitrate.
" .....	—	<b>N<sub>6</sub>O<sub>12</sub>Fe<sub>2</sub>o<sup>VI</sup></b>
		Diferrie hexanitrate.
<b>SO<sub>2</sub>Ho<sub>2</sub></b> .....	<b>SO<sub>2</sub>HoNa<sub>o</sub></b> .....	<b>SO<sub>2</sub>Na<sub>o</sub></b>
Sulphuric.	Hydric sodic sulphate.	Sodic sulphate.
" .....	—	<b>SO<sub>2</sub>Ba<sub>o</sub></b> "
" .....	—	Baric sulphate.
" .....	—	<b>S<sub>3</sub>O<sub>6</sub>Al<sub>2</sub>o<sup>VI</sup></b> , 18OH <sub>2</sub>
" .....	—	Aluminic sulphate.
" .....	—	<b>S<sub>4</sub>O<sub>8</sub>Ko<sub>4</sub>Al<sub>2</sub>o<sup>VI</sup></b> , 24OH <sub>2</sub>
		Dipotassic aluminic tetrasulphate.
		(Common potash alum.)
<b>COHo<sub>2</sub>?</b> .....	<b>COHoNa<sub>o</sub></b> .....	<b>CONa<sub>o</sub></b> , 100H <sub>2</sub>
Carbonic.	Hydric sodic carbonate.	Sodic carbonate.
" .....	<b>COHoAm<sub>o</sub></b> .....	<b>COAm<sub>o</sub></b>
" .....	Hydric ammonic carb...	Ammonic carbonate.
" .....	<b>C<sub>2</sub>O<sub>2</sub>Ho<sub>2</sub>Cao</b> " .....	<b>COCao</b> "
	Hydric calcic carbonate	Calcic carbonate.
<b>SiHo<sub>4</sub></b> .....	—	<b>SiGlo</b> " <sub>2</sub>
Silicic (tetrabasic)		<i>Phenacite</i> (Diglucinic silicate).
" .....	—	<b>Si<sub>2</sub>Al<sub>2</sub>o<sup>VI</sup>Cao</b> "
		<i>Anorthite</i> (Aluminic calcic disilicate).

<sup>1</sup> This formula corresponds to the production of nitric acid from nitrogen, tetroxide, and hydroxyl.

<sup>2</sup> Corresponding to the synthesis of this salt from N<sub>2</sub>O<sub>4</sub> and PbO<sub>2</sub>.

Acid.	Acid Salt.	Normal Salt.
<b>SiOH<sub>2</sub></b> .....	—	<b>Si<sub>2</sub>OMgo"</b>
Silicic (dibasic)	.....	<i>Enstatite</i> (monomagnesian silicate).
" " .....	—	<b>Si<sub>2</sub>O<sub>3</sub>Cao" Mgo"</b>
" " .....	.....	<i>Diopside</i> (calcic magnesian disilicate).
" " .....	—	<b>Si<sub>6</sub>O<sub>6</sub>Al<sub>3</sub>O<sup>vi</sup>Glo<sup>3</sup></b>
		<i>Emerald</i> (Trigluccinic aluminic hexa-silicate).
<b>POH<sub>3</sub></b> .....	<b>POH<sub>2</sub>NaO<sub>3</sub>, 12OH<sub>2</sub></b> ...	—
Phosphoric (Tribasic)	Hydric disodic phosphate.	
" .....	<b>POH<sub>2</sub>NaO<sub>3</sub>, OH<sub>2</sub></b> .....	<b>PO NaO<sub>3</sub>, 12 OH<sub>2</sub></b>
	Dihydric sodic phosph. .	Trisodic phosphate.
" .....	<b>POH<sub>2</sub>AmoNaO<sub>3</sub>, 40OH<sub>2</sub></b>	—
	Hydric ammonic sodic phosphate.	
	(Microcosmic salt.)	
" .....	<b>P<sub>2</sub>O<sub>3</sub>Ho<sub>4</sub>Cao"</b> .....	<b>P<sub>2</sub>O<sub>3</sub>Cao<sup>3</sup></b>
	Tetrahydric calcic diphosphate.	Tricalcic diphosphate.
		(Bone ash.)
<b>PO<sub>2</sub>Ho</b> .....	—	<b>P<sub>6</sub>O<sub>12</sub>Fe<sub>2</sub>O<sup>vi</sup></b>
Metaphosphoric acid (Monobasic.)		Ferric metaphosphate.
" " ...	—	<b>PO<sub>2</sub>NaO</b>
		Sodic metaphosphate.
<b>P<sub>2</sub>O<sub>3</sub>Ho<sub>4</sub></b> .....	<b>P<sub>2</sub>O<sub>3</sub>Ho<sub>2</sub>KO<sub>2</sub></b> .....	<b>P<sub>2</sub>O<sub>3</sub>Nz<sub>4</sub></b>
Pyrophos. acid. (Tetrabasic.)	Dihydric dipotassic pyrophosphate.	Sodic pyrophosphate.

Formulae may also be written in a manner still better calculated to display the constitution of the compounds represented. Thus plumbic nitrate, of which the graphic formula is—



may be written symbolically  $\left\{ \begin{array}{c} \text{NO}_2 \\ \text{Pbo} \\ \text{NO}_2 \end{array} \right.$  In this notation the bracket

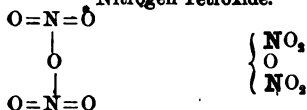
always signifies that the elements and radicals placed perpendicularly with regard to each other are in direct combination. The use of the bracket is further shown by the following examples:—

Graphic Formulae.	Symbolic Formulae.
Cl—O—O—O—H	$\left\{ \begin{array}{c} \text{OCl} \\ \text{O} \\ \text{OH} \end{array} \right.$

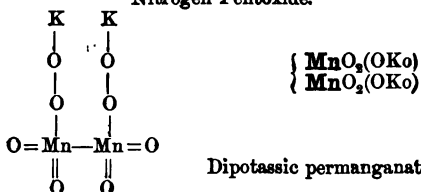
## Chloric Acid.



## Nitrogen Tetroxide.



## Nitrogen Pentoxide.

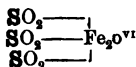
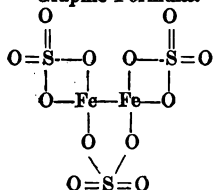


## Dipotassic permanganate.

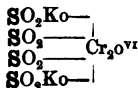
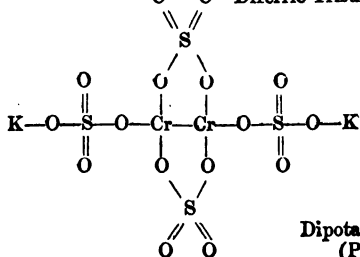
Another method of indicating the manner in which the bonds are distributed is sometimes adopted in the case of very complex formulae. Examples are given below:—

## Graphic Formulae.

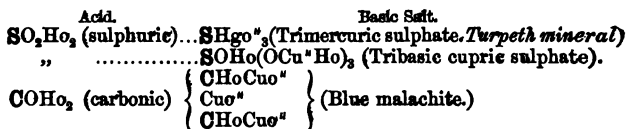
## Symbolic Formulae.



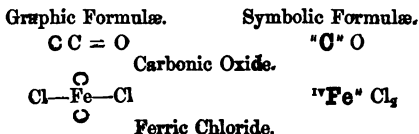
## Diferric Trisulphate.

Dipotassic dichromic tetrasulphate.  
(Potassium chrome alum.)

Dr. Frankland thus defines a basic salt: "When the number of bonds of the metal or compound positive radical contained in a salt exceeds the number of atoms of displaceable hydrogen in the acid, the compound is usually termed a basic salt." Examples:—



Latent bonds are indicated in this notation by atomicity marks placed to the left of the symbol; atomicity marks on the right of the symbol indicate active bonds. Thus—



These indicators of latent atomicity are, however, only used where two atoms of the same element are joined together, as in ferric chloride:—



and also in cases "where two or more atoms of the same element are joined together under such circumstances, that the number of bonds uniting them cannot be found by subtracting the co-efficient of active atomicity from the absolute atomicity of the element; as in hydric persulphide ( $\text{S}'_2\text{H}_2$ ), for instance, which might otherwise be viewed as  $\text{S}'_2\text{H}_2$  or  $\text{S}_2\text{H}_2$ ."—"Lecture Notes," vol. i. p. 23.)

For the further development of this notation the student is referred to the "Lecture Notes," or to the paper in the "Journal of the Chemical Society," for September, 1866.

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London, 1871.

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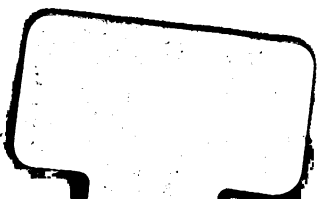
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